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The Mechanisms of Pyrolysis, Oxidation, and Burning of Organic Materials

UNITED STATES DEPARTMENT OF COMMERCE • Peter G. Peterson, *Secretary*
NATIONAL BUREAU OF STANDARDS • Lawrence M. Kushner, *Acting Director*

The Mechanisms of Pyrolysis, Oxidation, and Burning of Organic Materials

Based on Invited Papers and Discussion
4th Materials Research Symposium
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Leo A. Wall, Editor

Institute for Materials Research
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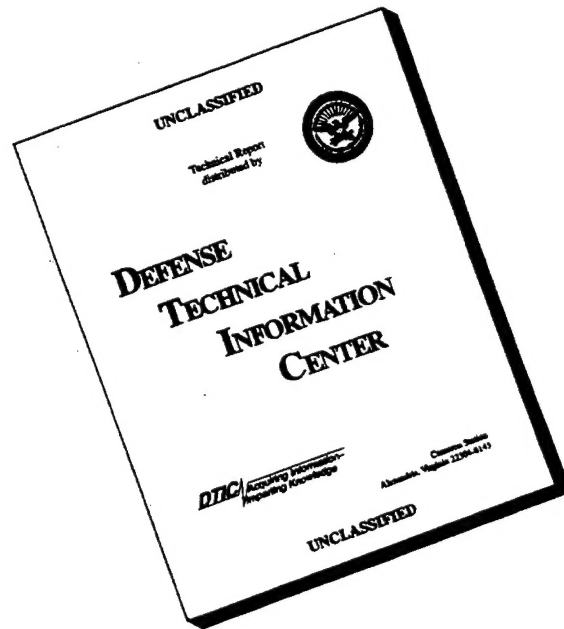
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Abstract

A symposium on The Mechanisms of Pyrolysis, Oxidation, and Burning of Organic Materials was held at the National Bureau of Standards in October 1970. This volume contains the nineteen papers presented and much of the discussion which followed.

These papers review and discuss the current status of kinetic studies on the reactions of organic materials in both gas and condensed phases. The topics covered include: pyrolysis of hydrocarbons, pyrolysis of polymers, oxidation of polymers, oxidation of organic compounds, burning of organic compounds and burning of polymers. Particular emphasis is placed on the elucidation of the mechanisms of reaction in terms of free radicals or other transient species and physical effects.

Key words: Burning; hydrocarbons; organic materials; oxidation; polymers; pyrolysis.

Foreword

The Institute for Materials Research of the National Bureau of Standards has among its responsibilities the investigation of the chemical and physical properties of materials, the development of metrological techniques for measuring such properties and characterizing materials, and the dissemination of data and information of importance for the advance of industry and commerce. In many important areas there are phenomena where measurement methods are nonexistent or inadequate, and where the critical properties needed for characterization of the process or material are not clearly identified. The burning of polymers, which is a complex process involving the pyrolysis and oxidation of polymers and their gaseous decomposition products, had for a time been in this category, but recent work has shown encouraging signs of definite progress.

We are therefore particularly pleased to have as the topic for our 4th Materials Research Symposium, "The Mechanisms of Pyrolysis, Oxidation and Burning of Organic Materials." It is also particularly timely because it is apparent that many of our most pressing and difficult national problems from solid waste disposal to product safety involve or require knowledge of the combustion, burning and deterioration of organic materials. This symposium was organized for the purpose of intensively reviewing, examining, evaluating and disseminating available knowledge and data on these complicated physical and chemical processes.

It is hoped that the publication of these proceedings will be of value to specialized investigators in the particular areas discussed, as well as those actively engaged in attacking such current problems as flammable fabrics, fire safety, air pollution, waste disposal, recycling of organic materials and the design of safe products.

Such problems will require considerable effort in utilizing science for the development, where possible, of technological solutions for social and national needs.

J. D. HOFFMAN, Director
Institute for Materials Research
National Bureau of Standards

Preface

This symposium, "The Mechanisms of Pyrolysis, Oxidation, and Burning of Organic Materials," germinated from a suggestion made about six years ago by Dr. Alvin S. Gordon of the Naval Weapons Center, China Lake, California, that a conference on both gas phase and condensed phase pyrolysis would be very productive. This idea then developed naturally to include oxidation and burning. Thus the symposium covers six areas of specialization or subdisciplines, all of which have the common thread of free radical reactions.

Starting with the historical paper by Professor F. O. Rice, this publication reviews and discusses the current status of the fields of gas phase pyrolysis, polymer pyrolysis, polymer oxidation, gas phase oxidation, gas phase burning, and the burning of polymers, with emphasis on the physical and chemical mechanisms of the processes.

The arrangement of the subject matter is intended to gradually and systematically introduce the reader to a very complex and relatively unexplored area of research, the burning of polymers or organic materials. It is also hoped that the organization of the various topics will stimulate new work, identify critical problems and lead to fruitful investigations.

The efforts and kind cooperation of the authors, discussants, and all the participants in this symposium are greatly appreciated.

LEO A. WALL
Editor and Chairman

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Francis Owen Rice

The career of Professor Francis Owen Rice as a chemist, scientist and educator covers over a half century. He was born in Liverpool, England on May 20, 1890 and studied at the University of Liverpool where he received the B.Sc. degree in 1911, the M.Sc. in 1912 and the D.Sc. in 1916. An 1851 Exhibition Fellowship brought him to Princeton University and the U.S.A. in 1919. After teaching at New York University, 1919–24, and Johns Hopkins University, 1924–38, he became Professor and Head of the Chemistry Department at Catholic University. Upon retiring from Catholic University in 1959 he served as Professor and Chairman of the Chemistry Department at Georgetown University till 1962, and then as Principle Research Scientist, Radiation Laboratory, University of Notre Dame, 1962–68. Since 1968 he has been a Fellow-by-Courtesy in the Chemistry Department at the Johns Hopkins University and also actively continues research in his home laboratory.

Professor Rice is best known for his trail-blazing work on transient free radicals and their role in the mechanism of organic reactions, such as pyrolysis, oxidation and burning. Subsequently he pioneered studies of trapped free radicals and utilized the results of his free radical studies in developing hypotheses for a rational explanation of extraterrestrial phenomena such as the colors of the planet, Jupiter. At the present time he is interested in the possibility of reacting solids by mechanical methods.

Thus it is particularly fitting and appropriate that Professor Rice presented the introductory paper at the symposium on the Mechanisms of Pyrolysis, Oxidation and Burning of Organic Materials.

The Genesis of Free Radical Chemistry

Francis O. Rice

Department of Chemistry, Johns Hopkins University, Baltimore, Md. 21218

Modern chemistry is a late-comer among the sciences and came into being only at the beginning of the 19th Century when the phlogiston theory was abandoned to be replaced by Dalton's Atomic Theory. As Dalton's Theory became firmly established there grew with it the belief known as the doctrine of valency which resulted, by the middle of the 19th Centry, in the denial of the very existence of free radicals.

In the early 20th Century, the work of many scientists—Hinshelwood, Bodenstein, Taylor—in the fields of photochemistry and kinetics led to the belief that free radicals not only existed but played an important part in the mechanism of chemical transformations. Paneth's discovery that free radicals could be detected by their removal of certain metallic mirrors was followed by Rice's demonstration that organic compounds did decompose thermally into free radicals, and then, the Rice-Herzfeld theory that showed it was possible to explain quantitatively the mechanism of the thermal decomposition of organic compounds. In *The Annual Review of Physical Chemistry* (1971) a chapter on Paraffin Pyrolysis contains the following sentence: "All in this field are now agreed that the reactions can basically be described in terms of the Rice-Herzfeld radical chain mechanisms and that, in general, chains are long."

Key words: Alchemy; free radicals; genesis; phlogiston; valency.

Among the sciences chemistry made a late start. Even at the end of the 1700's when its sister sciences—mathematics, physics and biology—had attained a modest degree of maturity, chemical transformations were explained on the basis of the mythical phlogiston. How could this have occurred? Except for medicine, chemistry is the most applicable of all the sciences and from this standpoint it might be supposed that its development would come about sooner than that of the other sciences. Doubtless in prehistoric days many chemical discoveries were made independently in different parts of the world and kept as closely guarded family secrets. Thus, the reduction of ores in fires, the formation of glass by fusion of pot-ashes with sand and the production of crude soap by hydrolysis of fats by hot aqueous potash solutions are all examples of discoveries that may well have been made before the dawn of history.

Although chemical history does not commence with Greek science, the Greeks really determined the early history of chemistry and unwittingly set it off in a wrong direction. We can detect three main lines of chemical thought among Greek philosophers:

(1) Ignoble and sordid, unworthy of written record, is every sort of scientific activity directed to use or profit. The foregoing quotation is a paraphrase of written thoughts of many Greek philosophers.

(2) To the mind trained in epistemology, dialectics, and etiology, the experiment is superfluous. The menial work of the experimentalist should be left to slaves and the common man.

(3) Properties are not inherent in a substance. By suitable manipulation properties may be modified so that a substance A may be endowed with all the properties of a substance B.

It should be realized that not all Greek scientists subscribed to all, or even to one, of these postulates. As with everything else, where large numbers are involved there is always a distribution, commonly known to chemists by the title of Maxwell's Distribution Law. There were notable experimenters among Greek scientists and glimmerings of Dalton's Atomic Theory appear in the writings of several Greek philosophers. However, by the beginning of the Christian era chemical opinion had crystalized fairly definitely along the three lines indicated.

Indeed there seemed evidence for all of them, especially the third. If one takes a piece of ordinary sulfur, a brittle yellow solid, and melts it, and continues heating until it almost reaches the boiling point, a thick, dark-reddish liquid results. When this liquid is poured into cold water, instead of getting back the brittle yellow sulfer, one obtains an amber-colored solid with the properties of rubber. Surely it was reasonable to think that one could take a cheap base metal such as lead and endow it, not only with the yellow color, but with all the other properties of gold. The period of alchemistry lasted for centuries, during which chemists struggled in vain to perform such feats as to change lead into gold. We know now that it is possible to change one element into another, but the technique is far beyond anything available to the alchemist—and the cost far outweighs the value of the product.

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Although alchemical work continued during the first ten or twelve centuries of the Christian era, iatrochemistry—the study of chemistry in medicine—developed simultaneously. The iatrochemists hoped to find a magic drug, the so-called philosophers' stone, that would cure all diseases and would indeed confer eternal life. Magic prescriptions and potions abounded, most of them without any merit whatsoever. However, here and there evidence appeared often in some quite nauseating prescriptions, that the search was not necessarily in vain. For example, among the hundreds of recommendations for treating infections, one was to make a poultice of the green mold on stale bread and apply it to the wound. This green mold is rich in penicillin!

About the middle of the 1600's there appeared the strangest theory of all, the Phlogiston theory—designed in the first place to explain the chemistry of burning. This wrong theory lasted until about 1800, the birth date of modern chemistry.

In order to understand the acceptance of the experimental work of Lavoisier and the theory of John Dalton, which at long last (about 1800 A.D.) set the mainstream of chemistry in the right direction, we have to go back many hundreds of years to the work of Roger Bacon, a Franciscian friar who lived in England during the 13th Century and is commonly regarded as the intellectual originator of the experimental method. However, it was only many centuries later that the experiment took its rightful place in natural science and in all disputes became generally accepted as the court of last resort. Even in the 16th Century the attitude of many scientists may be illustrated by an extract from the writings of a Frenchman, Jean Rey. He was considering the question, whether matter could be made to disappear during the course of a chemical transformation, and wrote "I affirm that the examination of weights that is made by the balance differs greatly from that made by reason. The latter is only employed by the judicious, the former can be practiced by the veriest clown; the latter is always exact; the former is seldom without deception." By an extraordinary piece of sophistry he "proved" (correctly) that matter does not disappear during the course of an ordinary chemical reaction.

The combination of the experimental work of Lavoisier and the theoretical work of Dalton resulted in a great flowering of the science, particularly of organic chemistry. However, in one vital area chemists were still misled: their work seemed to disprove the very existence of free radicals. The doctrine of valency became generally accepted. Hydrogen was monovalent, oxygen divalent, nitrogen trivalent, and carbon tetravalent. The existence of hydrogen peroxide, hydrazine, ethylene and acetylene could be explained readily by writing respectively
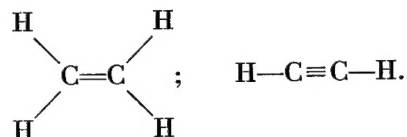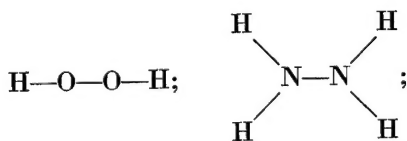
The existence of CO and the many metallic salts obviously of different valencies, was more difficult to explain, but even here the idea of latent or "sleeping" valencies gave an acceptable explanation.

Even Kekulé's formula for the structure of benzene fitted into the valency theory. If one writes benzene as (A) with fixed double bonds, there should be two ortho disubstituted compounds, (B) and (C); however, only one could be found. Kekule must have had some sort of intuitive understanding of what we now call resonance when he postulated the migrating double bond to explain the existence of only one ortho disubstituted benzene.

(A)

(B)

(C)
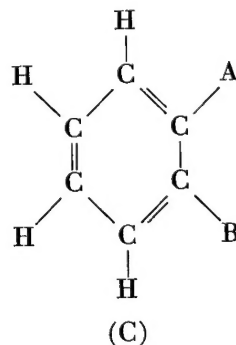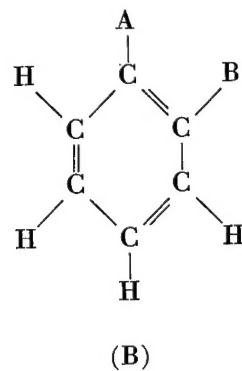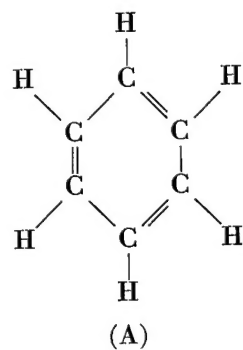
The situation in chemistry at the end of the 19th Century may be illustrated by a quotation from the

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eminent physical chemist Ostwald [1][1]: "It took a long time before it was finally recognized that the very nature of the organic radicals is inherently such as to preclude the possibility of isolating them." However, some few chemists persisted in considering the possibility that free radicals did exist and play a part in chemical reactions. Nef [2], in a series of papers published in the 1890's, concluded that a wide variety of organic transformations could be explained by postulating the intermediate formation of a divalent carbon radical. At that time little was known about relative bond strengths, and many of his proposed mechanisms are actually completely impossible.

The situation during the first two decades of the 20th Century may be illustrated by the following extracts from chemical textbooks published during that period:[2] "The assumption of the existence of radicals, capable of existing alone and playing a special role in chemical reactions, has long been abandoned." "It is evidently quite out of the question to isolate free alkyl groups." "Alkyl radicals do not exist independently. They occur only in combination with other elements or groups." "Carbon is quadrivalent, and on this foundation the whole superstructure of organic chemistry rests."

It is ironical that during the first part of the 20th Century physicists, especially spectroscopists, not knowing at all that free radicals did not exist, were actively investigating them. Their interaction with electromagnetic fields (wave lengths of absorption or emission, intensities and widths of lines) and the general theoretical understanding of the potential energy curve of two particles, made it possible to obtain with great accuracy for diatomic particles the equilibrium distance and the energy of dissociation. Unfortunately, at that time there was not the close liaison between physics and chemistry which exists today.
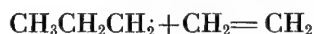
Since free radicals are short-lived entities, it is not surprising that chemical evidence of their existence was first pointed out by kineticists. Bodenstein in Germany, studying the hydrogen-chlorine reaction, finally became convinced that the mechanism of the reaction could best be described by an atomic chain. Hinshelwood, in England, succeeded in explaining the complicated mechanism of the hydrogen-oxygen reaction by a chain mechanism involving free radicals.

However, it was not until 1926 that experimental evidence for the existence of free radicals was first described [3]. Taylor and Jones [4] found that pure ethylene heated in a quartz flask at 260 °C remained stable indefinitely. However, when a mixture of ethylene and either mercury or lead alkyls was heated under the same conditions, a reaction occurred resulting in the formation of oils. Taylor and Jones explained the results by postulating

a primary dissociation of the metal alkyls:

$$Pb(CH_3)_4 \rightarrow Pb + 4CH_3;$$
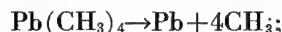
followed by reaction of the methyl radicals with ethylene as follows:

$$CH_3 + CH_2 = CH_2 \rightarrow CH_3CH_2CH_2;$$

$$CH_3CH_2CH_2 + CH_2 = CH_2$$

$$\rightarrow CH_3CH_2CH_2CH_2CH_2 \qquad etc.$$

Combination or disproportionation of the radicals resulted in the formation of oils. Although this work did not give any conclusive proof of the existence of free radicals, the explanation of Taylor and Jones proved to be essentially correct and was a significant factor in gaining acceptance for the existence and importance of free radicals in chemistry.

Just a few years later (1929) a paper appeared by Paneth and Hofeditz [5] showing how the methyl radical could be isolated and studied. Their method was to carry tetramethyl lead in a stream of an inert gas at low pressure, passing the gases through a furnace and at the end of the furnace bringing them in contact with a cold lead mirror. They thus showed conclusively that the tetramethyl lead decomposed into lead and methyl radicals. The latter combined with the cold lead mirror, reforming tetramethyl lead. Although the work of Paneth and Hofeditz seemed quite conclusive, it did not by any means gain general acceptance immediately. This was partly because the experiment itself is difficult: the lead mirror must be quite clean, and the flow of the gases, owing to the short life of the methyl radical, must be very rapid. Also, about a year after publication of the original paper, there appeared a paper by Muller and Schultze [6] suggesting that in the Paneth and Hofeditz experiment the removal of the lead mirror was merely due to the formation of hydrogen atoms.

Paneth [7] lost no time in replying and it seems worthwhile to illustrate the climate of the time by giving two extracts from his paper:

(1) "It will be shown that the experiments of Messrs. Schultze and Muller do not constitute any proof against the existence of free methyl."
(2) Footnote: "It is a fact well known among logicians that the undependability of such a conclusion is very easily recognized when it leads to an absurdity. As a striking example of their erroneous logic we may give the following example: All geese have 2 legs. This girl has 2 legs. Therefore it follows that this girl is a goose."

My own interest in free radicals started two or three years after I joined the Department of Chemistry at The Johns Hopkins University in 1924. Hinshelwood [8] had already studied the kinetics of the thermal decomposition of acetone and found that the decomposition followed a unimolecular law. He assumed that the decomposition was represented by

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[1] Figures in brackets indicate the literature references at the end of the paper.
[2] Since these quotations are taken from ephemeral literature, references are not given. However, these or similar statements may be found in every chemical textbook published during this period.

the equation

$$CH_3COCH_3 \rightarrow CO + C_2H_6$$
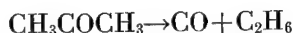
One of my students and I (9) soon found that the decomposition of acetone was really represented by the equation

$$CH_3COCH_3 \rightarrow CH_2 = CO + CH_4$$

At that time chemists thought that organic transformations occurred through a series of migrations of atoms or radicals, without the intermediate formation of free radicals. Thus, the thermal decomposition of acetone into ketene and methane would be represented by the migration of a hydrogen atom from one methyl group of the acetone molecule to the other, followed by rupture of the acetone molecule, thus producing ketene and methane.

This seemed to me to be asking a rather impossible behavior of a hydrogen atom. In the gaseous state, at atmospheric pressure or lower, an acetone molecule spends most of its time out of range of the force fields of other molecules. It seemed reasonable to assume that the heat energy flowing into the molecule would finally result in the rupture of the weakest bond, with the consequent formation of two free radicals, which would then fly apart and each react with the surrounding acetone molecules. It turned out that considerations of this kind, guided by our knowledge of bond strengths and the principal of least motion,[3] led to a chain reaction which gave the products ketene and methane. Having established the theory for acetone, it was easy to test it by comparing the theoretically predictable products of decomposition of hydrocarbons, other ketones, ethers, etc., with those actually produced experimentally. Such comparisons showed that free radical mechanisms provided a satisfactory explanation for the thermal decomposition of aliphatic organic compounds.

However, when the theory was first proposed we had no evidence at all of the actual existence of free radicals, during the thermal decomposition of organic compounds, and there thus was little hope of gaining acceptance of our postulated mechanisms. It was at this very time, when we needed it most, that the paper by Paneth and Hofeditz [5] appeared. To be sure, they had only discovered a method of detection of CH_3 radicals by their removal of lead mirrors, and it remained for us therefore to determine that the thermal decomposition of ordinary organic compounds, such as hydrocarbons, ketones, ethers, etc., resulted in the formation of free radicals. Our experiments were successful, and we found that all these compounds readily decomposed in this manner. We thereupon published the results of our work [11].

In the years that followed, the reception accorded our interpretations is best illustrated by such excerpts as the following:

(1) From a paper by R. E. Burk [12]:
"The thermal decomposition of straight chain

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paraffins is of outstanding interest for at least two reasons. Firstly, the reactions are basic ones in the technical "cracking" of petroleum fractions, practiced on a huge scale; secondly, since the C—C bonds are probably all alike energetically, straight chain paraffin molecules are almost ideal ones for mechanical and statistical calculation of reaction rates ... A paper on the decomposition of paraffins has just appeared, in which the first step is assumed to be free radical formation. The decomposition of radicals themselves

$$CH_3CH_2CH_2CH_3 \rightarrow 2CH_3CH_2$$

was thought to play an important part ... It seems unlikely that free radicals should be formed by thermal decomposition of hydrocarbons, because reaction 24 can occur with the evolution of some 70,000 or 100,000 calories, and with no

$$CH_3CH_2 + CH_3CH_2 \rightarrow C_2H_6 + CH_2 = CH_2$$
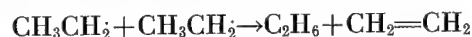
evident kinetic impediment, before the radicals leave the sphere of reaction."
(2) From a paper by Kassel [13]:
"The decomposition of paraffin hydrocarbons has been discussed by F. O. Rice and by Burk; Burk upholds the view that a paraffin is split out in the initial act, while Rice assumes free radical formation. Both attempt to obtain evidence from the composition of the reaction products but without any very striking successes." – – – "There is a second explanation for the results of Rice and Evering. It seems possible that the primary process in these reactions may be of the type

$$CH_3CH_2CH_3 \rightarrow CH_4 + CH_3\overset{\diagup}{\underset{\diagdown}{C}H}$$
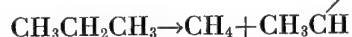
This view has the advantage that the methyl group in splitting off captures a hydrogen atom from the carbon to which it was itself attached, rather than from a more distant atom, as is the case when ethylene is the initial product ... It is likely that

$CH_3\overset{\diagup}{\underset{\diagdown}{C}H}$ would behave like a free radical in a Paneth

test such as used by Rice and Evering."
(3) Still another extract may be given: Simons and Dull
"On the Reaction of Gaseous Methyl with Carbon Tetraiodide" [14].
"... the identification of these as free radicals (odd molecules) is still open to question ... Its reaction with carbon tetra-iodide to form methyl iodide is an argument against the assumption of Kassel that the active particles are alkylidene radicals, for in that case di-iodomethane should have been formed."

It finally became obvious to organic chemists that free radicals were important intermediaries in many organic transformations. There remained, however, the problem that troubled physical chemists, principally kineticists, that thermal decompositions of organic compounds followed simple laws, of the first

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[3] These matters were clarified in a later paper by Rice and Teller [10].

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or second order, and this seemed quite impossible on the basis of the mechanisms I was proposing.

Fortunately for me, at that time a colleague in the Physics Department, Karl Herzfeld, was also interested in reaction mechanisms. Together we made an examination of the free radical theory which I had proposed, with the object of finding out what kind of kinetics it would lead to. It turned out that the problem was a very messy one algebraically, but our calculations finally led to a simple solution, depending on the chain ending [15]. It was found that thermal decompositions such as, for example, that of acetone, should follow a unimolecular law, whereas the thermal decomposition of acetaldehyde should follow a 1.5 order. It was actually found that published data for the latter reaction fitted better a 1.5 order of decomposition than a second order. We submitted this paper to the American Chemical Society for publication and it seems worthwhile to give some extracts of our correspondence with the late Professor Arthur B. Lamb, who was then editor. Comments of referee I (in part):

"The paper is important and is concisely and rather elegantly expressed; and I have concluded that I should recommend its publication in full ... The concept of free radicals in kinetics is a very live subject now, and in my opinion this paper is a distinct contribution to this field."

Professor Lamb submitted the paper to another scientist who preferred not to act as a referee and wrote:

"... I know that we should be criticized for publishing such a long paper with so many equations and I believe it would be better to have the judgement of another referee."

The comments of the other referee were as follows (in part):

"I am very decidedly of the opinion that the material involved should be published, but I cannot agree with the judgement of your first referee that it is concisely expressed ...

... So far as this particular paper is concerned, I think you would be justified in requiring that it be shortened by 10 to 12 pages."

Then followed the Editor's decision (in part):

"There is no question as to our desire to publish this manuscript as a valuable contribution to the subject of free radicals ... I am glad to accept your manuscript for publication provided it can be condensed from its present 27 typewritten pages to not over 17 typewritten pages."

The Editor's decision posed quite a problem for us, which we solved in the following manner. We went over the paper carefully, but succeeded in shortening it only by several pages. As it was necessary to retype the paper, and as we were unable to shorten it by the required 10 pages without emasculating it altogether, we resorted to the use of a typewriter with somewhat smaller type, and used narrower margins. In this way we met the Editor's requirements.

The publication of the Rice-Herzfeld paper [15] removed the final objections to the theory and thereafter the progress of free radical chemistry proceeded exponentially.

It is extraordinarily difficult to select for mention any names among those of the many distinguished scientists who contributed to the advance of free radical chemistry. However, there are a few lines of free radical research that call for special mention. About 1932 I had become interested in the methylene radical and my former student, Glasebrook, and I [16] discovered that although it does not combine with metallic lead it can be studied through its combination with tellurium. We had no notion at the time of the properties of this extraordinary particle and it remained for the physical chemist, George Kistiakowsky [17], at Harvard and the organic chemist, Doering [18], then at Yale, to uncover its properties.

At Rochester W. A. Noyes, Jr. [19] founded a school interested principally in a study of the photochemical production of free radicals. The work of Porter and Norrish, in England [20] demonstrated that it was possible through flash photolysis, actually to obtain the spectra of free radicals.

Lastly the work of Dr. E. W. R. Steacie [21] at Ottawa should be mentioned. Canada does not have as many centers for free radical research, nor does it produce a volume of work as great as do some other countries, but in proportion to its population and wealth its production far outranks every other country; this is due in large measure to the foresight and planning of E. W. R. Steacie.

Finally, since this is essentially an historical paper, we should ask ourselves "what will future historians have to say concerning free radical science today?" What will scientists think, 200 years from now, when reading the papers presented at this meeting? Are we going in the right direction? Have we finally arrived, by and large, at a true and full understanding of free radical reactions? In my estimation, the answer will be NO.

As an example, for many years I have had a feeling of uneasiness when reading papers describing measurements of the speed of chemical reactions, in which it is mentioned that the surface of the vessel must be "conditioned" before reproducible results could be obtained. However, reproducibility can hardly be regarded as a safe criterion of truth: the phlogiston theory gave consistently reproducible results—which were exactly opposite to the truth.

There is a second Rice-Herzfeld paper [22] in which this matter is discussed. There is the possibility that chains may start from the wall, go out into the gas phase and terminate on the wall.

Only a few decades ago the difficulties of travel were such as practically to preclude a Symposium such as this, which provides an opportunity for scientists from far distant countries to engage in informal discussion. Out of such deliberations are likely to emerge many new lines of attack on the challenging and important problem of controlling the pyrolysis, oxidation and burning of organic materials.

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Pyrolysis of Organic Compounds in the Gas Phase

Alvin S. Gordon and R. H. Knipe

Research Department, Chemistry Division, Naval Weapons Center, China Lake, Calif. 93555

A critical review of the pyrolysis of organic compounds is made. The review is divided into hydrocarbons, halides, and oxy compounds. Most hydrocarbon reactions have an important unimolecular component, either the initial step in the case of chain reactions (e.g., saturated hydrocarbon decomposition) or a one step reaction which may involve a transient biradical structure. There are many types of pyrolysis reactions in the latter category.

For halocarbon pyrolysis there are two reaction paths, one involving an unimolecular rupture of the carbon-halogen bond and the other an unimolecular elimination of the hydrogen halide molecule via a polarized activated complex. The preferred path is determined by the self-quenching efficiency of the radical path. If highly efficient, the molecular elimination path will dominate and vise versa. In some systems, the two paths are competitive.

Oxy hydrocarbons such as acids and esters pyrolyze via the polarized complex molecular elimination path. Ethers appear to pyrolyze via a free radical chain mechanism while ethylene oxide is initiated by a unimolecular rearrangement to acetaldehyde with excess energy. The vibrationally excited molecule can decompose into two radicals and initiate chain decomposition.

Key words: Decomposition; kinetics of decomposition; pyrolysis of hydrocarbons; radical mechanisms; unimolecular decomposition; molecular mechanisms.

1. Introduction

It is fair to inquire how the pyrolysis of organic compounds is related to flamibility of organic materials. The relation is that when organic materials burn in a diffusion flame, the condensed phase is heated by the flame and provides gaseous molecules, with and without decomposition of the organic material; these gaseous molecules form the fuel for the flame. It has been demonstrated that the fuel molecules inside the flame mantle are extensively pyrolyzed with only a trivial amount of oxygen being present and probably acting as an efficient catalyst [1, 2].[1]

The gross aspects of the pyrolysis of most organic compounds were delineated by F. O. Rice in the early 1930's [3]. For the bulk of such molecules, the reaction is initiated by the breaking of the weakest C—C bond to form two radicals. These radicals and their daughter radicals, abstract an atom from the parent compound to produce product molecules and new radicals in a chain mechanism. In the case where large radicals are formed, these will isomerize to other radicals as well as pyrolyze by unimolecular reactions to olefins and smaller radicals. The chain reactions are quenched by radical–radical combination and disproportionation reactions.

In addition to the above chain decomposition reaction, organic molecules may decompose in a unimolecular reaction to give two molecules without free radical intervention. Other reaction paths are unimolecular isomerization and bimolecular re-

actions involving one or two reactants. For these last processes, the Woodward-Hoffman orbital correlation rules have been able to provide simple rationalizations of the products in many cases [4]. Usually, one of the many possible mechanisms dominates. Bond strengths, molecular structure and polar effects have been used to explain why a particular mechanism is dominant in a given temperature range.

For crystalline solids, the pyrolysis reaction rate may be determined at the interface between reacted material and the unreacted crystalline material as well as by reactions in the solid volume. For liquids, because of their comparatively high dielectric constants, the competitive reactions may include ionized species which are unlikely in gas phase reactions except at temperatures well above 1000 K. In condensed media the original two radicals, formed by decomposing a molecule remain in close proximity for a period of time because of hindrance to diffusion. This "cage" effect leads to higher radical–radical reaction rates than for the same average radical concentration uniformly distributed.

In this paper we shall restrict our review to homogeneous gas phase reactions and include examples of hydrocarbons, halocarbons and some oxygenated compounds. Although we recognize that pyrolysis reactions of economic significance such as occur in flames, production of commercially useful hydrocarbons from petroleum feedstocks, and lampblack manufacture all involve very deep pyrolysis, we shall focus on the early stages of reaction before secondary and higher products play any significant role.

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[1] Figures in brackets indicate the literature references at the end of this paper.

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2. Unimolecular Reactions

Since unimolecular reactions are so prominent in the gas phase decomposition of organic molecules, they have received much theoretical and experimental attention. There is an extensive recent review of thermal unimolecular reactions of hydrocarbons and we will attempt not to extensively overlap with this work [5].

Grossly, a thermal unimolecular reaction is a consequence of an occasional molecule acquiring enough energy to undergo chemical change as a result of collision with other molecules in its environment. If the collision rate is sufficiently rapid relative to the rate of reaction of these energetic molecules, their steady state concentration will approximate the limiting Maxwell-Boltzmann distribution with the result that the rate of reaction at a particular temperature is a linear function of the concentration of reactant molecules. At lower collision rates the concentration of sufficiently energetic molecules falls significantly below the Maxwell-Boltzmann value with an accompanying "fall-off" in the rate of reaction. The pressure at which "fall-off" becomes significant decreases as the complexity of the molecule increases. As the temperature is increased, the pressure at which "fall-off" becomes significant increases. At flame temperatures, "fall-off" will be of importance for unimolecular reactions involving even moderately complex molecules.

Because of the principle of microscopic reversibility, the pressure independence of the rate of breaking a bond also applies to the making of a bond under the same conditions. The experimental demonstration that the rate of ethane decomposing to two methyls is first order in ethane concentration, indicates that under the same conditions two methyls combine without need for a third body. Because of the thermodynamic relationship involving the forward and reverse elementary reaction, it is often more convenient to study the reverse reaction to generate information about the forward reaction. Thus, Benson and Bose have studied the bimolecular addition of HI to olefins in order to gain insight into the unimolecular decomposition of alkyl iodides [6].

There are two general approaches that have been widely employed to fit experimental data on unimolecular reactions. The statistical approach is exemplified by the RRKM formulation [7]. The stochastic approach has been diversely applied to non-thermal initiation of chemical reaction [8] and as a tool to investigate the limits of validity of the statistical approach [9]. The Marcus improvement on the older RRK approach consists of using the actual molecular frequencies and anharmonicities where they are known and replacing the empirical frequency factor by an Eyring-like transmission coefficient for the activated molecular states [10]. As a consequence, the RRKM formulation leads to ostensibly apriori estimates of the high pressure limit of the unimolecular rate constant which correspond to the estimates of transition state theory as well as fitting "fall-off" with decreasing pressure.

There remains an element of adjustability in that the molecular degrees of freedom are divided into adiabatic (do not contribute energy to the process) and active. The "fall-off" behavior is influenced by the manner in which this division is made. Also, the frequencies and/or anharmonicities in the activated molecules are not precisely known and hence may be subjected to empirical variation to adjust both the high pressure limit and the "fall-off" behavior. The "fall-off" behavior can be further adjusted by variation of the collision efficiency. Recently, it has been shown that for the case of thermal isomerizations, inclusion of back reaction from excited isomer configurations can lead to descriptions of the "fall-off" behavior with physically more acceptable collision efficiencies that would otherwise be necessary [11].

A major disadvantage of the RRKM approach over the RRK is the complexity of the computations which necessitates the use of large scale computers. The advantage is that it is possible to obtain a description of the "fall-off" in the unimolecular rate constant which may be valid over a considerable range of temperature [12]. More sophisticated treatment of the mechanics of the dissociation process suggests that parametric adjustments used in fitting the observed kinetics may reveal some qualitative features of the nature of the excited molecular configuration which is undergoing reaction [13, 14]. However, it must be recognized that the principal value of the RRKM approach is in correlating available data. The wide variability possible in RRKM estimates of "fall-off" behavior has recently been illustrated for methyl radical combination by Casas et al. who suggest that the data for this reaction should be fit with a somewhat tighter activated complex than had been previously supposed [15].

$$\longrightarrow \quad CH_2 = CH - CH = CH_2$$
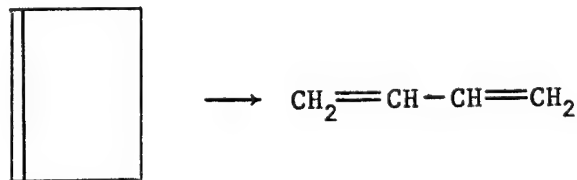
In what follows we will discuss the pyrolysis of various types of hydrocarbons which follow a unimolecular path. For cyclic saturated hydrocarbons, the pyrolysis path is overall molecular, although a transient biradical intermediate may be involved. The simplest type of reaction which involves electronic rearrangement may be illustrated by the work of Hauser and Walters on cyclobutene pyrolysis [16]. A C—C bond breaks and the electrons rearrange to form 1,3 butadiene. The cooperative reaction has an $A = 10^{13.26}$ s^{-1} and $E = 32.7$ kcal/mole.[2]

The preexponential factor corresponds to a small entropy change in going to the activated complex,

indicating the complex is cyclic with no additional degree of rotation over the normal molecule.

Frey and co-workers have pyrolyzed vinyl cyclopropane and alkyl substituted vinyl cyclopropane.[5] In all instances there is no evidence of any H migration but an isomerization initiated by opening the allylic $C=C$ bond; e.g.,
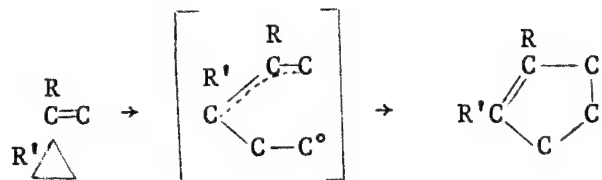
where R and R' may be an H or an alkyl group. All these reactions are unimolecular with $E \sim 50$ kcal/mole, and $A \sim 10^{14}$ s^{-1}. The presence of the allylic C—C bond lowers the energy of activation over opening a cyclopropane ring. If it is assumed that all the allylic energy is in the activated complex, which is quite unlikely, then a value for the allylic resonance of 13–15 kcal/mole may be obtained by comparison of the energy of activation for opening the non-allylic and the allylic ring. It would be perhaps more realistic to say that the value is the minimum allylic energy. The rotational energy of the vinyl group is lost when going to its resonance stabilized activated complex, thus causing a negative entropy of activation. The activated complex of cyclopropane has less hindered rotation than that of vinyl cyclopropane with a resulting higher pre-exponential factor. Pyrolysis of the isomer of vinyl cyclopropane, methylene cyclobutane has also been investigated. The molecule cannot easily rearrange to cyclopentene and falls apart unimolecularly to allene and ethylene.

Another class of molecular isomerizations which are closely related to vinyl cyclopropane isomerization are the sigmatropic rearrangements which involve the migration of a sigma bond flanked by one or more double bonds. The Cope rearrangement is an example of such a rearrangement. It may be illustrated by the reaction
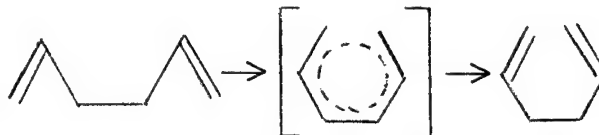

In a cooperative process, C_1 and C_6 atoms bond while the C_3—C_4 bond is broken and the electrons rearrange. Since some rotational degrees of freedom are lost in going to the cyclic activated complex, the entropy of activation is negative [17, 18]. The reaction mechanism is easily followed by using deuterium marked 1,6 groups in the reactant or by using an appropriately alkyl substituted compound. Typically, $A \sim 10^{11}$ s^{-1}, and $E \sim 36$ kcal/mole.

If C—H bonds are in the right configuration to be abstracted cooperatively with an electronic shift, then the molecule will rearrange in a unimolecular reaction analogous to the Cope rearrangement. A typical example of many reactions that have been studied is [19].
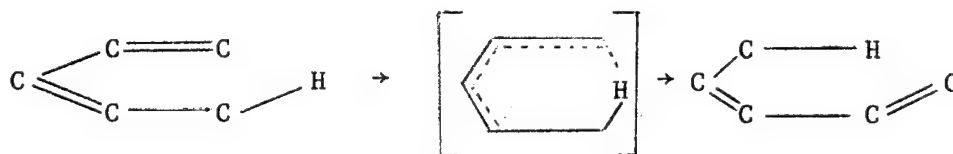
For these reactions typically $A \sim 10^{12}$ s^{-1} and $E \sim 35$ kcal/mole indicating, as would be anticipated, that the formation of the cyclic activated complex reduces the number of free rotations and results in a negative entropy of activation. These reactions are similar to the Cope rearrangement in that both cases involve a cyclic activated complex in which one bond is broken and another made with associated electronic rearrangement. In both of these cases there is little or no ΔH of reaction; hence the rates of the forward and backward reaction are the same.

Cyclopropane pyrolysis has been extensively studied. The kinetic data may be interpreted as resulting from the intermediate formation of a biradical by scission of one of the C—C bonds or the reaction path may be via an expanded ring. We will examine the biradical mechanism first.

Since the opening of the ring is over 60 kcal endothermic, any subsequent rate processes with a much higher rate constant such as the 1,2 H shift to form propylene occurs very rapidly in the thermal environment necessary for the formation of the biradical. A most informative study of cyclopropane has been reported by Rabinovitch, Schlag, and Wilberg [20]. It involved the geometrical isomerization of cis 1,2-dideutero cyclopropane which exists in the cis and trans form because H (or D) atoms cannot rotate through the ring. They studied the simultaneous geometrical and structural isomerization and found that the overall energy of activation for the geometric is 1.3 kcal/mole lower than for the structural while the preexponential factor for the geometric isomerization is about seven times that for the structural. Benson has interpreted these data in terms of the same slow step in both processes which is the opening of the ring to form a trimethylene biradical. This allows free rotation of the methylenes [21].

The 1,2 H shift from trimethylene to form propylene has a low E_{act} (calculated) of about 9.5 kcal/mole. On the other hand, Jackson and McNesby

showed that 1,2 H shift in *n*-propyl radicals did not complete with C—C bond scission, [22] while studies of a similar reaction of ethyl radicals in our laboratory indicates that the 1,2 H atom shift is about 10 percent of the loss of H atom at 500 °C [23]. The striking difference in the behavior of various 1,2 H shifts may be related to the ΔH of the reaction.

The difference in the heats of formation of the biradical and cyclopropane at about 450 °C (a convenient temperature for cyclopropane pyrolysis studies) is about 56 kcal/mole. On the other hand the experimental energy of activation is about 64 kcal/mole, indicating that the trimethylene has an energy about 8 kcal/mole less than the activated complex, so that the trimethylene must climb an 8 kcal/mole barrier to reform the ring. Since the back reaction must be many times faster than the forward, the two species are likely to be in equilibrium. The various reaction paths are

$$\triangle \underset{1}{\overset{2}{\rightleftarrows}} \overset{\bullet}{CH_2}CH_2\overset{\bullet}{CH_2} \xrightarrow{3} CH_3CH{=}CH_2$$
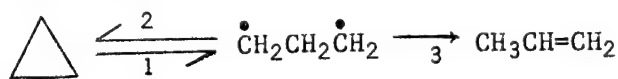
From the $\Delta S°$ of the reaction and the experimental preexponential factor for the forward reaction as well as the above data, k_2 and k_3 are readily calculated [24]. The various self consistent specific rate constants are

$$k_1 = 10^{16}10^{-64000/4.6T},$$

$$k_2 = 10^{13}10^{-8200/4.6T},$$

$$k_3 = 10^{12.2}10^{-9500/4.6T}$$

It should be added that an equally consistent set of kinetic parameters can be formulated if it is assumed that the trimethylene biradical plays no role, but that the activated complex allows free rotation and is the species which leads to both geometric and structural isomerization. Rabinovitch et al. refer to such an activated complex as an expanded ring.
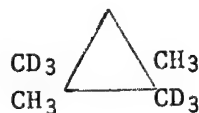
Two papers in the recent literature [25, 26] attempt to resolve the two mechanisms, one group by a study of

$$\begin{array}{c} CD_3 \diagup\!\!\triangle\!\!\diagdown CH_3 \\ CH_3 \diagdown\!\!\diagup CD_3 \end{array}$$

and the other group by using

$$\begin{array}{c} CH_3 \diagup\!\!\triangle\!\!\diagdown H \\ H \diagdown\!\!\diagup C_2H_5 \end{array}$$

In these compounds the change in optical activity is used to gain details of the mechanism. One team [25] concludes that much of the reaction path is via an expanded ring, while the other workers [26] conclude that the biradical path is most likely.

It should be noted that all the above types of unimolecular processes are isomerization reactions, mainly structural and some geometrical. Many important unimolecular cyclic hydrocarbon pyrolysis reactions occur either by a cooperative process to give final products, or by breaking C—C bonds. This process may proceed via biradical or expanded ring cooperative processes which are not readily differentiable as noted for cyclopropane above. Examples of reactions giving products in one step are illustrated below.

The pyrolysis of *cis* and *trans* 1,2 dimethyl cyclobutane are examples of unimolecular reactions which result in molecular products [27]. Various simultaneous reactions may be studied: formation of ethene and butene-2, formation of 2 moles of propene, and isomerization of the parent compound. Also, the butene-2 may be analyzed for *cis* and *trans* components. The kinetic parameters for the various reactions paths are listed below:

	A (s^{-1})	E (kcal/mole)
Cis→Trans	$6.4{\times}10^{14}$	60.1
Trans→Cis	$3.7{\times}10^{14}$	61.3
*Cis→*Ethane+Butene-2	$3.7{\times}10^{15}$	63.0
*Trans→*Ethene+ Butene-2	$2.9{\times}10^{15}$	63.4
*Cis→*Propene	$3.0{\times}10^{15}$	60.4
*Trans→*Propene	$2.8{\times}10^{15}$	61.6

Unlike the cyclopropane (and dimethyl cyclopropane) pyrolysis, the rate of isomerization of the parent compound is much slower than the rate of formation of products. The butene-2 product largely reflects the steric configuration of the 1,2 dimethyl cyclobutane precursor.

Although Woodward-Hoffman rules are favorable for the reaction going by a biradical mechanism and unfavorable for a cooperative cleavage to final products, the qualitive prediction does not take into account that the paths may have different endothermicity. Thus, the ΔH reaction $\simeq$40 kcal/mole for a cooperative ring break to final products is consistent with the observed E_{act} of over 60 kcal/mole. This path would be stereospecific. For the biradical path there would be a competition between the back reaction to reform the cyclobutane ring and the breaking of the C—C bond to form two olefins. The back reaction to reform the ring has a negative entropy of activation while that to break the C—C bond is zero or positive. Additionally, the back reaction, by analogy with trimethylene going to cyclopropane, has a 5–7 kcal/mole barrier, while the breaking of the C—C bond has a barrier very close to zero. Therefore, the C—C bond break should be many hundreds of times more rapid than the reforming of the cyclobutane ring. When the biradical is in the activated complex configuration to form the olefins, it may have some olefinic character hindering the rotation around the C—C bonds which preserves the original isomer configuration. Thus both the cooperative expanded ring and the biradical decomposition paths are consistent with the results.

The elimination of molecular hydrogen from a hydrocarbon is a rare process. It has been quite well

established in a number of compounds such as cyclopentene, and 1,4-cyclohexadiene. For cyclopentene,
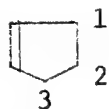
pyrolysis of the deuterium compound marked on the 3 position has shown that most of the elimination is 1,3 rather than 1,2 [28]. The results are in accord with the predictions of the Woodward-Hoffman orbital correlation rules [4]. The 1,2 elimination is predicted to involve H atoms which are *trans* to each other and thus must react through the ring as well as a 4 membered cyclic activated complex. Such a reaction is very difficult compared with the 1,3 which involves elimination of *cis* H's from a six membered cyclic activated complex.

1,4-cyclohexadiene has been shown by a number of investigators to pyrolyze cleanly to benzene and molecular H_2, while 1,3-cyclohexadiene is much more stable to pyrolysis and seems not to eliminate molecular H_2 [29, 30, 31]. Steric considerations for both the 1,3 hydrogen elimination from cyclopentene and hydrogen elimination from 1,4-cyclohexadiene suggest that the activated complex must involve considerable structural distortion.

The Woodward-Hoffman rules have been used to rationalize the products from a variety of unimolecular reactions [32]. Orbital correlation has not been widely considered relative to radical reactions. Longuet-Higgins and Abrahamson have discussed the case of the cyclopropyl radical, ion and cation.[33] Since for either the disrotary mode or the contrarotary mode a change in the overall symmetry of the electronic ground state is involved in the isomerization of cyclopropyl radial to the allyl radical, these authors suggest that the reaction should have a large activation energy. McNesby and Gordon have presented evidence that this isomerization does in fact proceed at an appreciable rate at temperatures below 400°C [34]. Relative to the symmetry consideration, H_2 elimination from the cyclopentyl radical is analogous to the disrotary cyclopropyl isomerization. Gordon has presented evidence for this reaction at relatively low temperature [35]. Thus, it appears that restrictions due to symmetry correlations may not be as severe for odd-number electron systems as for the even-number electron system.

## 3. Halo and Oxy, Carbon-Hydrogen Compounds

The pyrolysis of alkyl halides have been reviewed recently by Maccoll [36]. The pyrolysis of alkyl fluorides goes at a high enough temperature so that the walls of the reaction vessel are strongly attacked, leading to difficulties of interpretation. Pritchard, et al. have shown that the reverse reaction forming an excited partially fluorinated ethane molecule via combination of two CH_2F radicals eliminates HF

and gives $CHF=CH_2$ [37]. It should be noted that this experiment is performed at room temperature and the C—C formed in making ethane has more than enough energy to surmount the energy of activation barrier for eliminating HF. The study involves super excited molecules relative to the thermal pyrolysis of 1,2 difluorethane. It is interesting that the analogous reactions of CH_3 radicals has never revealed the slightest evidence of H_2 elimination from the excited ethane, even though both thermal processes are quite analogous. It can be concluded that there is a fundamental difference in the mechanism for HF and H_2 molecular eliminations from a molecule. As will be seen below, HCl, HBr, and HI are molecularly eliminated from the corresponding alkyl halides as is the organic acid from an ester when pyrolyzed. Both xanthates and carbonates also pyrolyze via molecular elimination.

A very striking factor in the pyrolysis of alkyl halides (methyl halide is a special case) is the large effect of substitution of a hydrogen on the α carbon atom (which contains the halogen) by an alkyl group. There is a much smaller effect of alkyl substitution on the β carbon. Maccoll and Thomas first pointed out that the homolytic bond ($RX \rightarrow R + X$) strengths of the various C—X bonds did not correlate with the energies of activation for elimination [38]. On the other hand, there is a strong correlation with the heterolytic bond dissociation energies ($RX \rightarrow R^+ + X^-$). Maccoll put forth the explanation that the activated complex was associated with a highly polarized C—X and some small polarization of the C—H of the 4 atom complex. Benson and Bose have extended the concept of Maccoll to a complex where the H and X have a one electron bond with formal changes of $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively [39]. Calculations based on the model including a polarization term as well as charge attraction and repulsion to give the minimum energy of the ion pair have resulted in values in moderately good agreement with observation. Benson and Haugen have tried to include molecular H_2 elimination in this model, but the experimental validation is not very convincing [40]. In addition, there is no evidence that an alkyl group substituted on the α carbon in hydrocarbons has the dramatic effect on pyrolysis parameters noted with alkyl halides.

The molecular elimination of HX is complicated by the possibility of a radical reaction initiated by a C—X scission. In his review, Maccoll quotes Barton and Oryon, and Howlett that a chain reaction is the preferred path for decomposition of a chloro compound [36, 41, 42]. Since the molecular elimination has a much lower E_{act} ($\sim$60 kcal/mole) than the breaking of a C—C bond ($\sim$80 kcal/mole), the radical reaction can only be favored by long chains resulting from the original break. It will decompose by the competitive molecular mechanism if the reactant or the products are strong radical quenching molecules, or if the preferred abstraction path leads to a radical intermediate which cannot stabilize itself by breaking a C—Cl bond. As an example, CH_2ClCH_2Cl decomposes via a radical chain because

$$Cl + CH_2ClCH_2Cl \rightarrow HCl + \dot{C}HClCH_2Cl$$

and
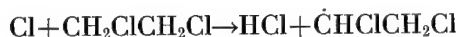
$$\dot{C}HClCH_2Cl \rightarrow CHClCH_2 + Cl$$
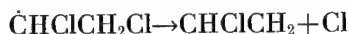
On the other hand, CH_2ClCH_3 and $CHCl_2CH_3$ decompose via molecular mechanisms since the preferred abstraction position on the parent results in $\dot{C}HClCH_3$ and $\dot{C}Cl_2CH_3$ radicals which cannot easily decompose to continue the chain. The last mechanism is substantiated by study of chlorine atom attack on ethyl chloride, resulting in 1,1 dichloroethane and 1,1,1 trichloroethane [43]. The ΔE_{act} for abstraction of H from the α and β carbon position thus strongly favors the α position. To account for the results at 600 K, we can say that at least 99 percent of the chlorine atoms must abstract an αH relative to a βH from the parent compound. Taking into consideration that there are 3 βH atoms and 2 αH atoms in ethylchloride
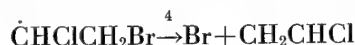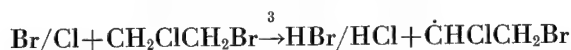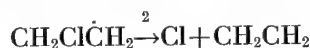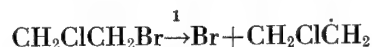
$$3/2 e^{-E_\beta/RT} < \frac{1}{99} e^{-E_\alpha/RT}$$

and

$$E_\beta - E_\alpha \geq 6 \text{ kcal/mole}$$

For the corresponding bromides, the radical chain process is favored over the molecular elimination, indicating that for Br abstraction of H from the α and β positions in CH_3CH_2Br kinetically is more favorable for the β position than for the corresponding chloro compound. When both chlorine and bromine are attached to carbon atoms, the rate of H abstraction by Br atoms for an analogous series are in the order $CH_3Cl > CH_3Br > CH_4$. A very recent paper on the kinetics of the thermal decomposition of 1 bromo, 2 chloro ethane is in line with the above observations [44]. The main products are HBr and CH_2CHCl formed via a radical chain:

$$CH_2ClCH_2Br \overset{1}{\rightarrow} Br + CH_2Cl\dot{C}H_2$$

$$CH_2Cl\dot{C}H_2 \overset{2}{\rightarrow} Cl + CH_2CH_2$$

$$Br/Cl + CH_2ClCH_2Br \overset{3}{\rightarrow} HBr/HCl + \dot{C}HClCH_2Br$$

$$\dot{C}HClCH_2Br \overset{4}{\rightarrow} Br + CH_2CHCl$$

The chain is then set up via reactions 3 and 4 and quenched by various radical–radical reactions.

For iodo compounds, it is likely that both a radical as well as a molecular mechanism path occur concurrently. Benson and Bose ingeniously studied the reverse reaction adding HI to an olefin to establish the unimolecular reaction for alkyliodide decomposition [39]. Analogous studies with olefins and HBr or HCl were not feasible because in the temperature region where these reactions occur with reasonable rates, the equilibrium is strongly on the side where the reactants predominate.

The pyrolysis of various organic esters of acetic and proprionic acid in the gas phase have been studied. The reactions are homogeneous and unimolecular resulting in an olefin and the acid as products.
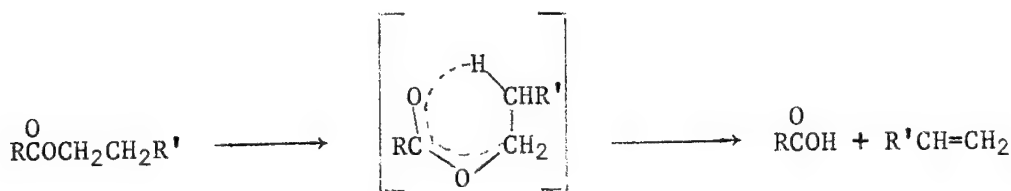
This reaction complex is a six-membered ring for elimination rather than the four-centered complex of the alkyl halides.

In a study of the pyrolysis of many acetates in the gas phase, Scheer et al. found that substitution of alkyl groups in the α position increased the decomposition rate much more than substitution in the β position [45]. The effect of substituting both H's in the α position by alkyl groups increased the rate by as much as almost 16,000 times the rate of the completely unsubstituted compound. Interestingly, the substitution of a second alkyl group increased the rate by as much as 200 times the rate for the mono alkyl substituted compound. This behavior, somewhat analogous to the molecular elimination reactions of alkyl halides, suggests very strongly that the activated complex is quite polar in nature. One interesting observation is that substitution in the α or β position of an electron withdrawing group (Cl) slows the rate of decomposition. This may be interpreted in terms of a large positive charge on the α carbon atom which donates the H atom, increasing the energy of the polar reaction complex.

There is one unanswered question: What is the effect of the methyl group on the carbonyl carbon? The question could be answered by studying the decomposition of a formic acid ester relative to the same acetic acid ester.

Gordon and Norris studied the pyrolysis of methyl-ethyl carbonate and diethyl carbonate [46]. The reaction is homogeneous and unimolecular and probably goes through a six-membered activated complex.

$$ROC\overset{O}{\overset{\|}{C}}OCH_2CH_3 \longrightarrow \left[\begin{array}{c} \text{...H} \\ \overset{O}{\underset{O}{ROC}} \overset{CH_2}{\underset{CH_2}{}} \end{array} \right] \longrightarrow ROCOOH + C_2H_4$$
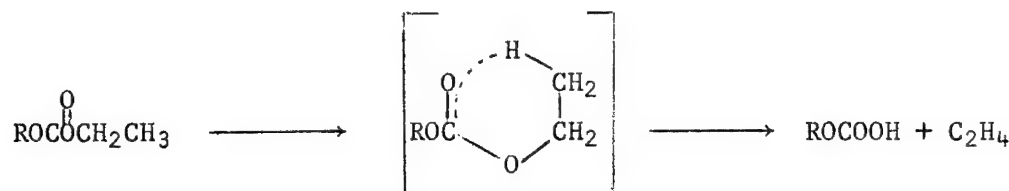
ROCOOH then decomposes to CO_2 and ROH, probably on the surface. Although the effect of substituents on the carbonyl containing carbon cannot be experimentally tested since $HOCOC_2H_5$ is

$$\overset{\|}{O}$$

not stable, this reaction by analogy also proceeds via a polar complex. Gordon and Norris saw no evidence that the hydrogen from the methyl group was transferred in dimethyl carbonate pyrolysis. It is not surprising because a more strained five-

membered complex would be involved in the reaction and the ΔH of the reaction would be about 65 kcal higher since no olefin would result.

Similarly the pyrolysis of Xanthates which also decomposes via a molecular mechanism probably occurs via a polar activated complex.

Laidler and McKenney have pyrolyzed diethyl and dimethyl ether [47]. For dimethyl ether, they found the reaction to be free radical initiated by a break of one of the C—O bonds. Diethyl ether was reported as being a combination of a free radical and a molecular elimination reaction.

$$C_2H_5OCH_2CH_3 \longrightarrow C_2H_5O \overset{H}{\underset{CH_2}{\overset{\diagup CH_2}{\rule{0pt}{1.5em}}}} \longrightarrow C_2H_5OH + C_2H_4$$
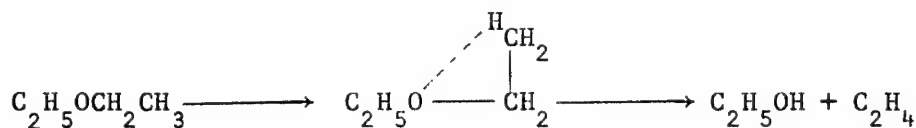
The pyrolysis of ethylene oxide resembles the initial step of cyclopropane pyrolysis.

for which $A = 10^{11.7}$ sec^{-1}, and $E = 30.6$ kcal/mole [50].

$$\overset{CH_2CH_2}{\underset{O}{\diagup \backslash}} \longrightarrow \overset{CH_2\dot{C}H_2}{\underset{O\cdot}{|}} \longrightarrow CH_3CHO*$$

The acetaldehyde may have as much as 85 kcal excess energy over thermal energy because of the exothermicity of the isomerization of the biradical. The excess energy coupled with the average thermal energy is more than enough to break the C—C bond. As was first noted by Neufeld and Blades and developed by Benson, the behavior of the pyrolysis of ethylene oxide may be rationalized as a combination of free radical reactions induced by the decomposition of the excited acetaldehyde and the stabilization of the acetaldehyde by collisions [48, 49]. The two processes explain the experimental behavior as a function of pressure and of temperature.

The Claisen rearrangement is analogous to the Cope rearrangement differing in that an oxygen atom replaces a carbon atom in the skeleton of the molecule. The rearrangement of vinylalkylether is a typical example:

4. Pyrolysis of Saturated Linear Hydrocarbons

Linear saturated hydrocarbons decompose by chain reactions, initiated by the unimolecular decomposition of the parent molecule into two radicals. For a chain reaction, the other elementary reactions in the mechanism can involve unimolecular, bimolecular and, for small radical–radical combinations, termolecular reactions.

The pyrolysis of a saturated hydrocarbon may be illustrated by ethane. Many studies of this reaction have been conducted with the mechanism generally agreed to be the following [51]:

$$C_2H_6 \rightarrow 2CH_3 \tag{1}$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \tag{2}$$

$$C_2H_5 + M \rightarrow C_2H_4 + H + M \tag{3}$$

$$H + C_2H_6 \rightarrow C_2H_5 + H_2 \tag{4}$$
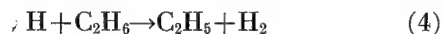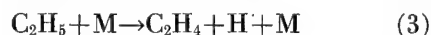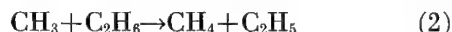
The reaction can be termined by

$$H + H + M \rightarrow H_2 + M \tag{5}$$

$$H + C_2H_5 + M \rightarrow C_2H_6 + M \tag{6a}$$

$$H + C_2H_5 \rightarrow H_2 + C_2H_4 \tag{6b}$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \tag{7a}$$

$$\rightarrow C_2H_6 + C_2H_4 \tag{7b}$$

13
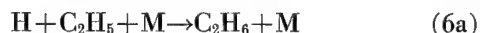
Of the termination reactions, the bimolecular combination of two ethyl radicals would have the largest rate constant since none of the reactions has any appreciable energy of activation and the other terminations are termolecular. In addition, the unimolecular pyrolysis of the ethyl radical has a fairly high energy of activation and is probably in its "fall-off" region in the temperature regime where ethane pyrolyzes, so that reaction (3) is much slower than reaction (4). Thus, the ethyl radical has the largest steady state radical concentration. Methane has been used to monitor the unimolecular ethane decomposition since it is completely stable in a temperature region where ethane pyrolyzes very rapidly. In our laboratory, we have investigated the effect of inert gases on the pyrolysis of ethane. These gases cause the overall rate of decomposition of ethane to increase appreciably; about 500 torr of Xenon pressure doubles the overall rate of ethane decomposition [52]. The decomposition of pure ethane has been shown in many laboratories, including ours, to be about first order relative to ethane disappearance, and the rate of formation of methane has been shown to be very closely first order in ethane concentration. The increase in overall rate by the addition of inert gases may be understood in terms of the pressure dependence of ethyl radical decomposition, as well as any effect of slowing the diffusion of H atoms to the wall where they may be quenched.

In any event, the H atom steady state concentration increases because this determines the rate of H_2 production (reaction 4) which is equal to the total rate of ethane decomposition within about one percent. However, we have also noted that the rate of methane increases by about ten percent under the same experimental condition in the presence of inert gases. There is no explanation for this in the mechanism noted above. The most likely reaction for the extra formation of methane is that between H and C_2H_5 radicals which are not stabilized because the C—C bond is about 85 kcal/mole, while the C—H bond is 98 kcal/mole, leaving 13 kcal/mole extra energy in addition to thermal energy which must be removed by collisions before the molecule can be stabilized. Rabinovitch and Setser have concluded from a theoretical study that there is a high probability that the excited molecule will split into two methyl radicales [53]. The extraneous source of methane clouds the experimental support for a preexponential factor of as much as 10^{17} for the unimolecular decomposition of ethane.

5. Bimolecular Mechanisms

For all of the radical chain reactions as discussed in the preceding section, after the original unimolecular scission of the reactant the resulting radicals (or their breakdown radicals) will abstract an atom from an unreacted molecule in a bimolecular reaction. This type of reaction is very important in most pyrolyses of organic molecules. There is an extensive literature of the kinetics of alkyl radicals, particularly methyl and perfluoro methyl, abstracting H as well as halo atoms [54].

Diels-Alder reactions have been extensively studied. They are bimolecular reactions between two olefin molecules, one of which must be a 1,3 diolefin to conform with the Woodward-Hoffman orbital correlation rules [4]. The activated complex is a six-membered ring:
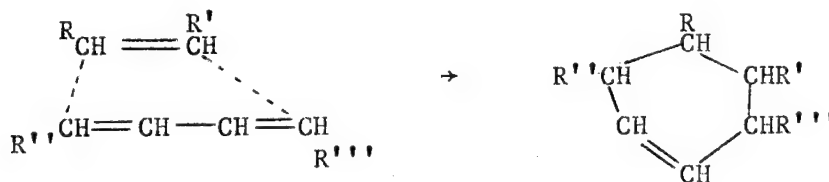
The pyrolysis rates of both olefins and acetylenes have been reported to be bimolecular. These reactions are discussed in the paper by Dr. M. Back.

6. Practical Pyrolysis Applications

In the work presented above, only the initial pyrolysis reactions were discussed. In a practical situation, such as the pyrolysis of hydrocarbon feed stocks to make more desirable hydrocarbons, or combustion reactions in a diffusion flame, reactions of the initial products will give rise to other products which will also participate, etc. All these products will also interact with the radicals formed in the original reactions giving rise to a most complicated situation. With the advent of computers with large capacities, it is possible to solve such an involved situation. Computer programs are now becoming commercially available [55]. The use of such programs requires that reliable kinetics for all the elementary steps be established. Such kinetic data is only attainable by careful studies of systems where secondary reaction complications are eliminated or controlled.

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Discussion

R. S. Konar (Catholic University):

Dr. Gordon has raised a serious question on the validity of the measurement of the initiation rate in ethane pyrolysis via the initial rate of methane formation in the uninhibited decomposition (i.e., before the radical–olefin reactions set in). According to his mechanism (p. 1 of preprints) CH_3 radicals are not only produced in the reaction (1), $C_2H_6 \rightarrow 2CH_3$, but also in the atom cracking reaction, viz:

$$H + C_2H_5 \rightarrow C_2H_6^* \rightarrow 2CH_3 \qquad (8)$$

$$C_2H_6^* + M \rightarrow C_2H_6 + M. \qquad (8a)$$
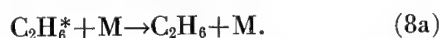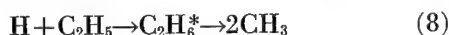
If the reaction (8) is really significant under the normal experimental conditions (at or above 100 torr C_2H_6, and at or above 540 °C), then in principle the measurement of total CH_4 at the initial stages would not be a measure of the initiation reaction

(1). However if the initiation reaction (1) is first order, and all the elementary reactions are homogeneous, then it is not clear how an inert gas can accelerate the rate of methane formation at a given pressure of the reactant. On the contrary, it should decrease the rate of CH_4 formation because of the occurrence of the reaction (8a). Dr. Gordon has found that the inert gas increases the rate of CH_4 production by about 10 percent. Does he refer to the initial rate of CH_4 formation? I wonder whether Dr. Gordon could illustrate this point in greater detail. Incidentally, it may be relevant to mention here that the calculations of Setser and Rabinovitz on ethane dissociation and on the recombination of CH_3 radicals (Adv. Photochem. **3**, 1, 1964) do not agree with the experimental data (Lin and Back, Can. J. Chem. **44**, 2360–61, 1966; Van Den Berg, Callear, and Norstrom, Chem. Phys. Letters **4**, 101, 1969).

It may be relevant to mention here that it has been found experimentally that diallyl is a product in the cadmium photosensitized decomposition of cyclopropane at 265 °C (Konar and Darwent, to be published) and it is believed that this diallyl is formed due to the interactions of allyl radicals originated almost entirely from the isomerization of cyclopropyl radicals produced in the system. This confirms the observation of McNesby and Gordon (page 11) that the isomerization of cyclopropyl radicals to allyl radicals does occur even below 400 °C, although this reaction is symmetry forbidden (Longuet-Higgins and Abrahamson, J. Am. Chem. Soc. **87**, 2045, 1965).

Alvin S. Gordon and R. H. Knipe:

Dr. Konar has raised the question of how a first order initial split of ethane and subsequent homogeneous elementary steps can effect the rate of the cracking reaction (8). If there is any effect of pressure he reasons that the cracking reaction should decrease because of reaction 8(a)

$$[C_2H_6^* + M \rightarrow C_2H_6 + M].$$
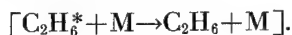
The answer to his question lies in reaction (3)

$$C_2H_5 + M \rightarrow C_2H_4 + H + M.$$

If this reaction is in its "fall-off" region in the pressure range of the studies, then increasing (M) will increase reaction (3), resulting in a higher steady state concentration of H atoms. The rate of H_2 formation is determined by reaction (4) and reflects the increased H atom concentration in the presence of inert gases, since the rate can be doubled with sufficient inert gas addition. The ethyl radical concentration, according to the mechanism is proportional to $(C_2H_6)^{1/2}$, independent of (M). Thus, reaction (8) increases proportional to (H) with changes in (M) for a given (C_2H_6). An interesting question which can be raised is why the rate of methane formation seems to be first order in ethane if the cracking reaction contributes? Here the (C_2H_5) is proportional to $(C_2H_6)^{1/2}$ and the (H) is independent of (C_2H_6) if no inert gases are present since the rate of H_2 is first order in (C_2H_6) and is formed via reaction (4). Thus, there is a component of CH_4 rate which is proportional to $(C_2H_6)^{1/2}$. The fact that it does not show experimentally is because it is not a high percentage of the total methane rate and is absorbed in the experimental error.

The above analysis is on the basis that reaction 8(a) in Konar's question plays only a minor role. It is difficult to evaluate the significance of reaction 8(a). Since the ethane molecule has about 98 kcal/mol plus its normal thermal energy and requires about 85 kcal/mol to break the C—C bond, it can survive a number of collisions and still have enough excess energy to break the C—C bond. In the paper we have referred to calculations by Rabinovitch and Setzer which predict that the $C_2H_5^*$ molecule is so short lived that it will not be quenched by collision. It is true, as pointed out by Konar, that calculations on the pressure at which recombination of methyl radicals becomes pressure dependent are not in accord with experiments, so that calculations of this type are not exact. There may be some quenching of the excited ethane, but our experimental results indicate that the cracking reaction is important in our pressure range.

Pyrolysis of Hydrocarbons

Margaret H. Back

Chemistry Department, University of Ottawa, Ottawa, Canada

Some current problems arising from studies of the pyrolysis of hydrocarbons are discussed and two stages of these studies are distinguished. The first stage concerns the description of the mechanism of the pyrolysis in terms of a series of elementary reactions. The types of reactions occurring during the pyrolysis of olefins are discussed from this point of view and the effects of temperature and pressure on these elementary reactions are shown to produce predictable changes in the over-all pyrolysis. Some problems in the mechanism for the pyrolysis of acetylene are discussed and a mechanism proposed which relates the reactions occurring in both the high and low temperature regions. The second stage in pyrolysis studies is attained when the mechanism of the reaction may be satisfactorily described in detail and experiments may then be designed to measure the rate constants of the elementary processes. Several studies on the paraffins have attained this goal and the results are examined for consistency with related measurements.

Key words: Acetylene; dissociation; elementary reactions; ethane; ethylene; hydrocarbons; kinetics; mechanism; methane; olefins; paraffins; propylene; pyrolysis; rate constants; unimolecular theory.

1. Introduction

The mechanisms by which hydrocarbons pyrolyze may be broadly divided into those which involve one elementary rearrangement process to give one or perhaps two products and those which include a series of radical reactions and yield several products. Ring compounds usually fall in the first category [1][1] and the large majority of straight and branched chain hydrocarbons fall in the latter group [2]. This discussion will be confined to the second class of mechanisms, those involving radical reactions.

Pyrolysis studies of the latter group may be considered to involve two stages. The first stage is the elucidation of the mechanism in terms of a series of elementary processes. Studies on the paraffins have, during the past several years, succeeded in completing this stage, with the notable exception of the simplest member of the series, methane, which still defies explanation on several aspects. When the elementary processes are known the system is ready for the second stage which involves the measurement of the rate constants for the elementary reactions. This stage constitutes the ultimate goal in pyrolysis studies, as perhaps in any kinetic study, where the measurement of an elementary rate constant and its variation with temperature and pressure may be considered the final achievement.

The discussion will begin with a brief review of some of the techniques used in pyrolysis studies and the relative merits of each. The paraffin systems will be discussed next, as examples of studies in stage two, and several measurements of elementary rate

constants will be described. Finally, the type of reactions occurring during the pyrolysis of the simple olefins will be described and compared with those occurring during the pyrolysis of acetylene.

2. Pyrolysis Techniques

The techniques used for pyrolysis studies are of three basic types, depending on the time resolution required for the experiments. The latter in turn is determined by the region of temperature where the reaction is studied. At temperatures up to about 900 K a static system may be used. The reactant is admitted to a vessel and the reaction allowed to proceed for a measurable time. For shorter reaction times, from approximately 1 to 0.01 seconds, a flow system is used and temperatures commonly range from about 900–1200 K. The technique of shock tube pyrolysis generally produces temperatures from 1000–2000 K and detection methods may have time resolutions as low as 10 μs.

Each method has its own limitations. The static system provides the most controllable conditions of temperature and reaction time but is most susceptible to surface reactions. The main problem in a flow system is the definition of the temperature profile and hence the time of the reaction. There is also the difficulty in obtaining a thorough test of the order of the reaction, since wide variations in the concentration of reactant are not usually feasible. An interesting flow system has been developed [3] in which the reacting gas is surrounded by a shell of inert gas, thus isolating the reactant from the walls of the reaction vessel. Measurements of the rate of the initiation step in the pyrolysis of neopentane were

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[1] Figures in brackets indicate the literature references at the end of this paper.

reported and shown [4] to be in reasonable agreement with previous studies in a static system [5].

Another interesting technique which has proved useful in measurements of elementary dissociation reactions and which may provide data on other fundamental processes is the very low pressure pyrolysis method developed by Benson and colleagues [6]. This technique uses a flow system with pressures sufficiently low that molecules are excited primarily by collisions with the wall. The rate of flow and hence the steady state concentration of molecules in the reactor depend on the rate of effusion from the orifice and can be accurately calculated. Measurements can be made over a wide temperature range and the method should provide useful tests for unimolecular theories. Several measurements of elementary rate constants have been made, among them the rate constants for dissociation and combination of allyl radicals [7], a result difficult to obtain by other methods.

Reactions in shock tubes are free of heterogeneous complications but have encountered difficulties in defining the temperature exactly and in describing the mechanism satisfactorily. Nevertheless several reliable measurements of rate constants for elementary reactions have been reported using the shock tube technique and among the hydrocarbon studies may be cited those of Tsang [8]. The special comparative technique used by Tsang allows the accurate measurement of relative rates but the absolute values depend on the accuracy of the measurements for the standard.

3. Parameters obtained from Pyrolysis Measurements

The measurement of the rate constant for an elementary reaction as a function of temperature gives an Arrhenius plot from which the activation energy and the frequency factor may be determined. In order to obtain the enthalpy change of the reaction the activation energy of the reverse reaction must be known. If the reverse reaction is a radical-radical reaction and its activation energy negligible then the measured activation energy will be within RT of the bond dissociation energy. The frequency factor gives an indication of the entropy change associated with the formation of the activated complex and allows some deductions about the structure of the complex.
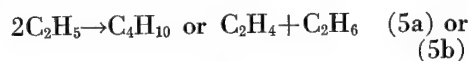
The interpretation of the kinetic parameters in this way depends on the assumption that the reaction occurs homogeneously. For a reaction occurring on the surface the parameters would have quite different meanings. The problem of surface reactions is a thorny one for most gas kineticists. The effects of heterogeneous reactions are often quite unpredictable and the various tests and treatments which have been used are sometimes ambiguous. The only case for which a meaningful test may be made is for the measurement of an elementary reaction. When the rate of an elementary reaction is measured any change in conditions of the reaction

will be immediately observable in the measurement if such changes affect the rate. If the concentration of surface sites is increased (as is usually done by packing the vessel) and the rate is unaffected then it may be concluded that the particular elementary reaction does not occur on the surface. Such tests may be quite ambiguous if a series of elementary reactions is involved, since each reaction may be affected in a different way at the surface and no net change may occur [9].

The comparison of rate constants over a wide range of temperature can provide useful information for tests of kinetic theories. The combination of results from the three techniques gives data spanning a very large temperature range. Of particular importance is data on rate constants in the pressure-dependent region. The existing theories, in particular the RRKM formulation [10], are able to describe adequately the variation of the first order rate constant with pressure [11], but the way in which the fall-off curves change with temperature provides a more stringent test for theories of energy transfer. Comparison of mechanism over a wide range of temperature can also be useful. Most mechanisms will be significantly altered by a change in temperature of one or two hundred degrees and if such changes can be predicted and confirmed experimentally, the mechanism may be well established.

4. Pyrolysis of Paraffins

Studies of the pyrolysis of the simple paraffins, with the exception of methane, have brought our understanding of these systems to a reasonably satisfactory stage. Much of this work has been done by Purnell, Quinn, and their co-workers at Cambridge and Swansea and by Niclause and colleagues at Nancy, France. The situation may be illustrated and summarized by the most thoroughly-studied paraffin, ethane [12–16]. The series of reactions which occur in the initial stage of the pyrolysis of ethane in the temperature range 800–900 K are as follows:

$$C_2H_6 \rightarrow 2CH_3 \qquad (1)$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \qquad (2)$$

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (3)$$

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \qquad (4)$$

$$2C_2H_5 \rightarrow C_4H_{10} \text{ or } C_2H_4 + C_2H_6 \qquad \text{(5a) or}$$
$$\text{(5b)}$$
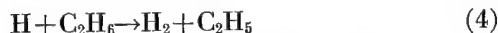
In this type of chain mechanism, initiation occurs by unimolecular dissociation of the reactant, the rate-controlling propagation step is the dissociation of a radical, and termination occurs by the bimolecular combination of radicals.

Similar mechanisms have been suggested for the pyrolysis of propane [17], butane [18], isobutane [19], neopentane [20, 21] and some C_6 to C_9 alkanes [22]. As the hydrocarbon becomes larger the number and variety of radicals increases and the variations on the propagation reactions, isomerization for

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FIGURE 1. *Arrhenius Plot of k_1.*

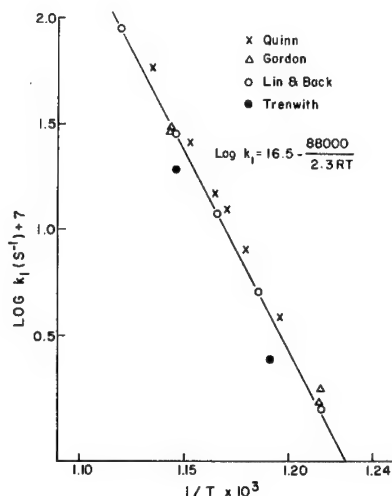example, can cause considerable complexity in the mechanism. Without summarizing all the arguments which led to the acceptance of these mechanisms I shall instead describe the measurements which have been made of some of the rate constants of these elementary reactions.

In the pyrolysis of ethane the following relations may be derived by applying the steady state treatment.

$$\tfrac{1}{2}R_{CH_4} = k_1(C_2H_6)$$

$$\frac{R_{H_2}}{(R_{C_4H_{10}})^{1/2}} = \frac{k_3}{(k_{5a})^{1/2}}$$

where R refers to the initial rate of formation of product. Measurements of the rate of formation of methane allow the determination of k_1 and measurements of the rates of formation of hydrogen and butane allow the determination of k_3, using the previously measured value for k_{5a} [23].

5. Measurements of k_1

Several measurements of the initial rate of formation of methane have been made as a function of temperature and of pressure. Considering the temperature variation first, figure 1 shows an Arrhenius plot of measurements by various workers. The maximum deviation from the line drawn is 40 percent and most of the measurements are within 20 percent. These measurements were made in static systems and the yield of methane as a function of time was extrapolated to zero time to obtain the initial rate. In spite of this close agreement the Arrhenius parameters obtained from each study show much wider variations.

Log A (s^{-1})	E Kcal/mole	Reference	Temperature range
16.3	86.0	Davis and Williamson	948–1048
17.45	91.7	Quinn	837–881
14.5	81.0	Gordon	748–873
16.00	86.0	Lin and Back	823–893
16.3	88.0	Trenwith	839–873

The rate of dissociation of ethane has also been studied as a function of pressure [24, 16]. The first order rate constant begins to decrease at pressures below about 100 Torr at temperatures above about 880 K. The experimental results have been interpreted with the RRKM theory [25] and a reasonable model for the activated complex has been found to give the observed variation of k_1 with pressure.

This dissociation reaction is important not only because it is the basic C–C bond but also because many measurements of the reverse reaction, the combination of methyl radicals, have been made, and since the equilibrium constant may be calculated with some precision the two rate constants may be compared over a wide range of temperature. The rate of combination of radicals has been measured in the range 300–776 K while the dissociation of ethane has been measured between 820 and 1050 K. Two aspects of this comparison are important: first the absolute magnitude of the rate constants in the high pressure region, and secondly the characteristics of the change in the first order rate constant with pressure.

Measurements of k_{-1} in the high pressure region in the temperature range 300–500 K gave a value of 2.2×10^{13} cm^3 m^{-1}s^{-1} [26, 27], apparently independent of temperature. An average of k_1 obtained from the pyrolysis of ethane,

$$\log k_1 = 16.5 - \frac{88000}{2.3RT}$$

together with the equilibrium constant gave a value for k_{-1} at 500 K of 3.8×10^{12} cm^3 m^{-1}s^{-1} [24]. The discrepancy of a factor of 6 is outside the estimated errors in each of the quantities k_1, k_{-1}, ΔS^0 or ΔH^0. The four measurements of k_1 in the range 820–870 K were within 50 percent of a mean and if this range is fixed for k_1 one cannot obtain a frequency factor for k_1 high enough to give agreement with k_{-1} without obtaining an unreasonably high value for E_1 and hence ΔH. The value of A obtained by Quinn [13] does agree with the measured value of k_{-1} but the activation energy of 91.7 kcal/mole implies a heat of formation of the methyl radical of 35.6 kcal/mole at 298 K which requires a value for D(CH$_3$–H) of 105.6 kcal/mole. It may be pointed that that any positive temperature coefficient of k_{-1} would make its value even greater at the temperatures at which k_1 was measured.

A similar discrepancy was observed in the study of neopentane. The average value for the rate constant for the dissociation of neopentane,

$$C_5H_{12} \rightarrow CH_3 + t - C_4H_9$$

from studies in the ranges 723–803 K [20] and 1070–1245 K [28] gave a rate constant for the reverse combination of radicals which was about 10 times less than the measured value for the combination of methyl radicals. The rate constant measured over the range 713–823 K [21], however, did not show this discrepancy but gave very good agreement with measurements of radical combinations.
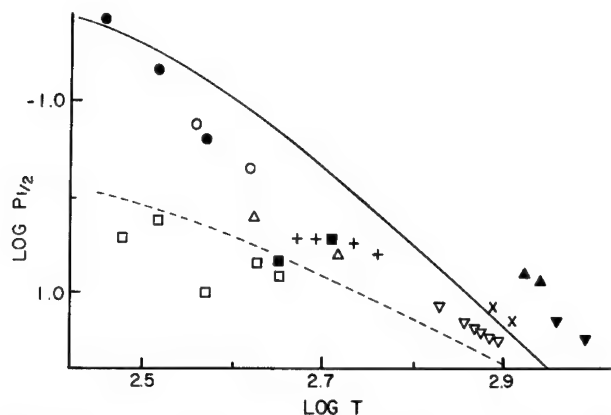
FIGURE 2. *Combination of methyl radicals; variation of the medium fall-off pressure with temperature.*

▼ [24]; ▲ [16]; X [30]; ▽ [31]; + [32]; △ [27]; ■ [26]; □ [33]; ○ [29]; ● [34].

It may be argued that the extrapolation of the rate constants measured in pyrolysis studies into a region of temperature so far from where they were measured carries with it enough error to account for the discrepancy observed. This is possible but still implies more error in the four quantities than is currently admitted. Such a wide temperature range is an exacting test for the validity of rate constant measurements and may help to reveal sources of error which might otherwise have remained hidden.

The measurements of the pressure dependence of the combination of methyl radicals over the temperature range 300–1000 K have been summarized by Casas, Previtali, Grotewold, and Lissi [29]. Their summary of the variation with temperature of the pressure at which the first-order rate constant has fallen to half its high pressure value is reproduced in figure 2. Grotewold and colleagues have shown that a transition state in which the free rotation of the methyl radicals, suggested by Rabinovitch and Setser [11] and designated by the dotted line, has been replaced by low frequency bending, designated by the solid curve, gives better agreement with their results at low temperature and also with the measurements in the higher temperature range. This model also reproduces the general shape of the curve of rate constant as a function of pressure obtained for the ethane dissociation. The values of $p_{1/2}$ obtained from the ethane pyrolysis are, however, still disturbingly far from the values obtained from the combination of methyl radicals.

The rate constants for the dissociation of isobutane and of neopentane have also been measured using similar techniques, and the results summarized as follows:

	log A (s^{-1})	E (kcal/mole)	Reference
Isobutane	17.8	82.5	19
Neopentane	18.1	85.9	21
	16.8	82.0	20

The high frequency factors appear to be characteristic of these dissociation reactions.

6. Radical dissociations

It had been suggested that the dissociation of the ethyl radical was pressure dependent in the temperature region of the ethane pyrolysis studies [13]. Measurements of the yields of hydrogen and butane from the pyrolysis of ethane confirmed this [15] and the rate constant obtained, extrapolated to the high pressure limit, agreed with that from the mercury photosensitized reaction of ethane over a lower temperature range [35].

The rate constant for the dissociation of the isopropyl radical into ethylene and a methyl radical was obtained from the study of the isobutane pyrolysis [36] and compared satisfactorily with the value measured in a lower temperature region [37]. Dissociation modes requiring higher activation energies are more easily measured in the higher temperature region of pyrolysis experiments while the rate requiring the lower activation energy is usually obtained from photolysis experiments in a lower temperature region.

These rate constants, of which only a few examples have been given, have been obtained with techniques and measurements which are not difficult. It is encouraging that simple methods can yield reliable and useful data.

7. Secondary reactions

The discussion so far has considered only those reactions occurring in the initial stages of the reaction, which means those reactions which do not involve any of the products. In the paraffin systems the olefin products react rapidly with radicals, producing secondary products and adding many new reactions to the mechanism [38]. This is a general consequence of forming products more reactive than the reactant and has caused considerable trouble in the studies of the paraffins. Most of the rate constants for the elementary reactions have been measured in the region where secondary reactions are not serious. Some attempts have been made to treat systems where the rates of formation of the products are changing with time [39], but because such systems generally involve a large number of elementary reactions very little quantitative data on rate constants can be obtained. Computer solutions to the equations may be the answer to this type of problem, although such solutions depend heavily on accurate data for the rate constants involved.

8. Methane

Since methane is the least reactive of the paraffins secondary reactions of the products become important at very early stages in the reaction, making studies of the primary reaction very difficult. The

overall course of the reaction may be written as follows:

$$2CH_4 \rightarrow C_2H_6 + H_2 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_2 + H_2 \rightarrow C + H_2$$

but the series of elementary reactions by which the products form has not been established [40]. No satisfactory measurement of the initiation step has been made in the lower temperature range of the studies in static and flow systems. Indeed, it has not been possible to identify the initiation step, partly because the two most likely possibilities,

$$CH_4 \rightarrow CH_3 + H$$

$$CH_4 \rightarrow CH_2 + H_2$$
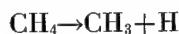
have very similar endothermicities. Studies in shock tubes [41, 42] have made the closest approach to measurements of the initiation step. Either of these initiation steps ought to show pressure dependence at fairly high pressures and hence could provide some interesting data for unimolecular theories. For identification and measurement of the initiation step the rate of formation of the primary products must be measured before secondary reactions become important. Perhaps the best hope for this is from the improved sensitivity of techniques for measuring products which may make it possible to study the decomposition of methane in the lower temperature range.
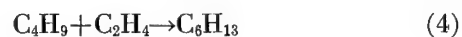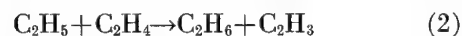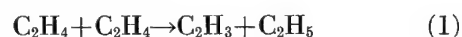
9. Pyrolysis of olefins

The thermal reactions of olefins are more complex than those of the paraffins but the general features of the mechanisms now seem moderately well understood. Both decomposition and condensation processes occur, yielding a wide range and variety of products. Induction periods are usually observed, at least in the lower temperature region. The kinetics are thus complex and quantiative measurements of elementary rate constants have not been reported from studies of the olefins.

Early work [2] on the pyrolysis of ethylene established that the rate of disappearance of ethylene was second order and the activation energy had the low value of 40 kcal/mole. The major products were propylene, butene-1, butadiene, ethane and polymer. A variety of minor products were reported depending on the extent of the reaction. Because an induction period was observed primary and secondary products were not always distinguished and the mechanisms suggested were somewhat speculative. The relative importance of radical and molecular processes was also uncertain.

Two recent studies of the thermal reactions of ethylene in the lower temperature region, 750–900 K, have provided a general framework for the mechanism of simultaneous polymerization and decomposition, although the results appeared at first to be conflicting. The first study by Halstead and Quinn (43), which covered the range 798–923 K and 10–270 torr, reported that all products showed self-acceleration and no changes in total pressure were

observed. They suggested the reaction was a degenerately branched chain reaction with butene-1 as the chain branching agent. The main chain propagating radicals were ethyl and vinyl and addition, decomposition and abstraction reactions of these radicals were able to account quantitatively for the time dependence of the yield of the major products.

The second study by Boyd, Wu, and Back [44] at somewhat higher pressures (150–600 torr) and lower temperatures (773–873 K) showed that ethane and a polymer were the only primary products and all other products were formed with an induction period. The formation of the polymer was deduced from the discrepancy between the measured pressure change and the pressure calculated from the measured products. The rate of formation of ethane was approximately second order with an activation energy of 42 kcal/mole. The mechanism suggested was a radical chain polymerization initiated by the bimolecular reaction of ethylene to give a vinyl and an ethyl radical. Initially the only two products were ethane and polymer.

$$C_2H_4 + C_2H_4 \rightarrow C_2H_3 + C_2H_5 \tag{1}$$

$$C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3 \tag{2}$$

$$\rightarrow C_4H_9 \tag{3}$$

$$C_4H_9 + C_2H_4 \rightarrow C_6H_{13} \tag{4}$$

$$\cdots\cdots\cdots\cdots$$

$$C_nH_{2n+1} + C_2H_4 \rightarrow C_2H_5 + C_nH_{2n} \tag{5}$$

$$C_2H_3 + C_2H_4 \rightarrow C_4H_7 \tag{6}$$

$$C_4H_7 + C_2H_4 \rightarrow C_6H_{11} \tag{7}$$

$$\cdots\cdots\cdots\cdots$$

$$C_nH_{2n-1} + C_2H_4 \rightarrow C_2H_5 + C_nH_{2n-2} \tag{8}$$

$$2C_2H_5 \rightarrow C_4H_{10}$$
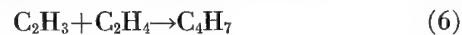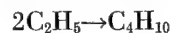
Subsequent decomposition of the unsaturated product formed in (5) and (8) led to the formation of the other products and the induction period observed was caused by the accumulation of sufficient unsaturated product in the system. The rate of formation of ethane, for a long chain process, is

$$R_{ethane} = k_2 (k_1/k_t)^{1/2} (C_2H_4)^2$$

The endothermicity of the initiation process is 65 kcal/mole so that the activation energy for formation of ethane is predicted to be about 40 kcal/mole, in satisfactory agreement with the experimental result.

The two mechanisms can be seen to be essentially complementary when the effect of pressure on each is considered [45]. The rate of the bimolecular initiation is proportional to the square of the concentration of ethylene, and at low pressures the secondary dissociation of higher molecular weight products will compete at an early stage. Also at low pressures the reversal of the addition steps will become increasingly important, the average molecular weight of the polymer will decrease and the yield of ethane in the initial stages will decrease. Thus the char-

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acteristics of the second study would change over to those of the first study as the pressure was lowered. The key difference between the two mechanisms is the extent of the polymerization that occurs before the dissociation of radicals competes with the addition, or dissociation of products creates a new source of radicals.

At the high temperature encountered in shock tube studies [46] polymerization does not occur, the vinyl and ethyl radicals rapidly dissociate and the major products are acetylene, hydrogen and butadiene. At first glance it might appear that a logical extrapolation of the low temperature radical chain mechanism could account for these products.

$$2C_2H_4 \rightarrow C_2H_3 + C_2H_5$$

$$C_2H_3 \rightarrow C_2H_2 + H$$

$$C_2H_5 \rightarrow C_2H_4 + H$$

$$H + C_2H_4 \rightarrow H_2 + C_2H_3$$

$$2C_2H_3 \rightarrow C_4H_6$$
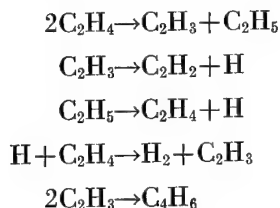
The observed activation energy of the rate (50 kcal/mole) is, however, lower than required by this mechanism (65 kcal/mole). A molecular process could occur at the high temperature of shock pyrolysis but would not explain the rapid formation of HD in experiments with mixtures of C_2H_4 and C_2D_4 (47).

10. Propylene

Polymerization occurs in the pyrolysis of propylene below about 550 °C but by 600 °C decomposition is the major process. The main products in the latter region are methane and ethylene and a variety of minor products of higher molecular weight is also formed [48]. As in the ethylene system an induction period was observed, and a radical chain mechanism appeared very probable. A recent study [49] showed that in the lower temperature region (740–820 K) in the initial stages of the reaction the distribution of products was simplified to methane, ethylene, propane and a group of C_6 compounds, and that initial rates of formation of these products were measurable before the onset of secondary reactions. The initial rates of formation of the C_6 products were second order in propylene with activation energies of between 45 and 50 kcal/mole. This suggested that the bimolecular reaction of propylene was the initiation process,

$$2C_3H_6 \rightarrow C_3H_5 + C_3H_7 \qquad (1)$$

and addition and abstraction processes of the allyl and propyl radicals could form the C_6 products observed. It was also shown that the rate of (1) was comparable to the rate of formation of the major products and it was concluded that the reaction in the initial stages was a radical non-chain reaction. In agreement with this, the activation energy for the rate of formation of the C_6 products was close to the activation energy for reaction (1) of 52 kcal/mole.

The reason for the difference in chain length from that in the ethylene system is that the bimolecular initiation reaction of propylene is much faster than the corresponding reaction of ethylene, and since the propagation reactions have similar rates the chain length should be much shorter in the propylene system. As in the ethylene system the dissociation of higher molecular weight products contributed to secondary initiation and the rate of formation of the more stable products increased rapidly after the induction period.

The reactions in olefin systems are dominated at low temperatures by addition reactions and as the size of the radical grows isomerization processes may occur, leading to a wide variety of products. In the propylene system 1-methylcyclopentene and 3-methylcyclopentene were major components in the C_6 fraction. It was suggested that cyclisation of the C_6H_{11} radical took place forming the methyl cyclopentyl radical, which then lost a hydrogen atom to form methylcyclopentene.
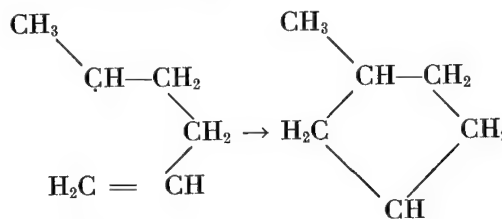
In the ethylene reaction benzene was a major secondary product and in this case the favourable cyclization process of the C_6 radical would be the formation of the C_6 ring rather than the C_5 ring.

A question arises concerning the reaction path for the bimolecular reactions of olefins. The process may be a simple hydrogen transfer reaction similar to disproportionation reactions of radicals, or it may involve the intermediate formation of a cyclobutane ring.

$$2C_2H_4 \rightarrow C_2H_3 + C_2H_5$$

$$2C_2H_4 \rightarrow c - C_4H_8$$
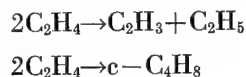
The rates of these two processes may be calculated using known thermodynamic and kinetic data [50]. In the case of ethylene the rate of formation of cyclobutane is about 300 times faster than the rate of formation of vinyl and ethyl radicals at 800 K and 600 torr, but in the case of propylene the two rates are almost identical. Whether cyclobutane may be an intermediate in the bimolecular reaction depends both on its rate of formation and on its rate of decomposition to yield the radicals formed by the reaction of the olefin. The simple cyclobutanes decompose almost exclusively by a molecular mechanism [51] and homogeneous dissociation into radicals has not been quantitatively measured. An empirical upper limit to the fraction of the decomposition of cyclobutane which gives radicals below 733 K was given as 0.1 percent. This makes the rate of formation of radicals from cyclobutane about three times less than the rate of formation of radicals from two molecules of ethylene at about 750 K. Given

the errors involved in measurement and calculations, it is just possible that radicals are formed through cyclobutane at this temperature.

In the propylene system the rates of the two reactions are about equal and since the formation of radicals in the decomposition of dimethylcyclobutane [52] was no more important than in the decomposition of cyclobutane the cyclic intermediate cannot contribute significantly to the formation of radicals in this system.

11. Acetylene

The mechanism of the acetylene pyrolysis has provoked much controversy, partly because of the difficulty of obtaining reliable data. Modern analysis has overcome much of this trouble and there is now general agreement concerning the natur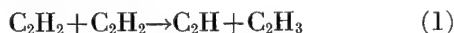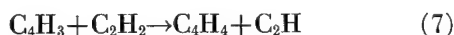e of the products under various conditions (53). Polymerization is dominant at low temperatures and as the temperature is increased ethylene, ethane, hydrogen, methane, vinylacetylene, diacetylene, benzene are among the products found in varying yields depending on temperature and conversion. In several aspects the acetylene pyrolysis bears a strong resemblance to the ethylene pyrolysis. The activation energy of the reaction is low, between 45 and 50 kcal/mole, and induction periods are observed. Both the initial rates and the maximum rates after the induction period are second order in acetylene. Most of the mechanisms suggest (54) that the initial step is a bimolecular reaction of acetylene to give an excited molecule of acetylene in the triplet state or a triplet or biradical species $C_4H_4^*$ [55]. The rate of formation of excited molecules in thermal systems, however, is somewhat uncertain; the frequency factor may be very low.

The bimolecular reaction of acetylene to give a vinyl and an ethynyl radical has been suggested [56], but has not been followed up with a complete mechanism. With this initiation the following reactions represent an outline of the most probable types of radical reactions which may occur during the pyrolysis of acetylene.

$$C_2H_2 + C_2H_2 \rightarrow C_2H + C_2H_3 \tag{1}$$

$$C_2H_3 \rightarrow C_2H_2 + H \tag{2}$$

$$C_2H + C_2H_2 \rightarrow C_4H_3 \tag{3}$$

High
temperature
$$C_4H_3 \rightarrow C_4H_2 + H \tag{4}$$

$$H + C_2H_2 \rightarrow H_2 + C_2H \tag{5}$$

$$2C_2H \rightarrow C_4H_2 \tag{6}$$

$$C_4H_3 + C_2H_2 \rightarrow C_4H_4 + C_2H \tag{7}$$

Intermediate
temperature
$$C_2H_3 + C_2H_2 \rightarrow C_4H_5 \tag{8}$$

$$C_4H_5 \rightarrow C_4H_4 + H \tag{9}$$

$$C_2H_3 + C_2H_2 \rightarrow C_2H_4 + C_2H \tag{10}$$

$$2C_4H_3 \rightarrow C_8H_6 \tag{11}$$

$$2C_2H_3 \rightarrow C_4H_6 \tag{12}$$

Low
temperature
$$C_4H_3 + C_2H_2 \rightarrow C_6H_5 \tag{13}$$

$$C_4H_5 + C_2H_2 \rightarrow C_6H_7 \tag{14}$$
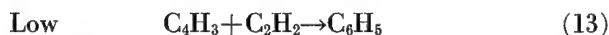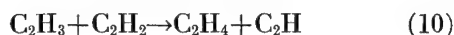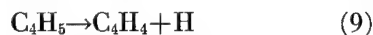
A mechanism similar to this in many respects was recently suggested by Cullis and Read [57]. They suggested initiation occurred by the following reaction:

$$2C_2H_2 \rightarrow C_4H_3 + H \tag{15}$$

Kinetically these two initiation reactions cannot be distinguished but reaction (1) is perhaps the simpler.

The products formed depend on the temperature region where the reaction occurs. At high temperatures, as found in shock tubes, decomposition will compete with addition and the C_4H_3 radical will disappear to form $C_4H_2 + H$. The vinyl radical will be largely dissociated. This region is illustrated by the work of Gay, Kistiakowsky, Michael, and Niki [58]. At lower temperatures the C_4H_3 radical may undergo abstraction to form C_4H_4, and reactions of the vinyl radical will become important. In this region vinylacetylene, ethylene and butadiene are products. At still lower temperatures further addition reactions will build up high molecular weight products.

Taking $\Delta H_f(C_2H)$ as 114 kcal/mole [59], $\Delta H_f(C_2H_3)$ as 64 kcal/mole, $S^0(C_2H)$ as 51. e.u. [60] and $\log k_{-1}(cm^3\ m^{-1}s^{-1}) = 12.5$ [23], the rate constant for reaction (1) may be expressed as

$$\log k_1(cm^3\ m^{-1}s^{-1}) = 15.0 - \frac{70000}{2.3RT}$$

Assuming a long chain reaction the rates of formation of the products may be expressed as follows.
(A) High temperature region:

$$\text{Rate } C_4H_2 = k_3 \left(\frac{k_1}{k_6}\right)^{1/2} (C_2H_2)^2$$

Taking reasonable values for reaction (3) [61], the activation energy of the rate is 40 kcal/mole and the frequency factor is $3 \times 10^{12}\ cm^3\ m^{-1}s^{-1}$. The activation energy is in reasonable agreement with the experimental value. The frequency factor is about a factor of 20 lower than suggested by Gay et al. [58], who averaged the results of ten different investigations but still fairly close considering the oversimplification of the mechanism.
(B) Intermediate temperature region:
Vinyl acetylene may be formed by either of the sequences (3) followed by (7) or (8) followed by (9), depending on the relative concentration of the C_2H_3 and C_2H radicals. In either case the rate-controlling propagation step will be the addition of the radical to acetylene.

$$\text{Rate } C_4H_4 = k_3 \left(\frac{k_1}{k_6}\right)^{1/2} (C_2H_2)^2$$

Thus in these two limiting cases represented by the

dominant formation of C_4H_2 or by C_4H_4 the rate expressions are the same or very similar.

(C) Low temperature region:

The primary products in this region are somewhat more uncertain but a general expression similar to those for the other regions may be written

$$\text{Rate polymer} = k_a \left(\frac{k_1}{k_t}\right)^{1/2} (C_2H_2)^2$$

where k_a is an average rate constant for addition and k_t represents the termination rate constant for the radicals involved.

Such a mechanism can therefore lead to a rate expression which will remain essentially the same over a wide range of temperature. The requirements are only that the addition of radicals to acetylene is the rate-determining step and that the termination steps involving the various radicals have similar rate constants. The mechanism is intended to show, not that excited molecules of acetylene may not be formed, but that there is no need to postulate their formation. First, the bimolecular initiation step can account for the low activation energy. Secondly, the rather erratic effects of surfaces observed may be expected in a long chain reaction where the propagation reaction of radicals may occur following adsorption on surface sites. Thirdly, the importance of cyclic compounds in the products, particularly benzene, is fully in accord with the present knowledge of the rapid cyclisation processes of radicals containing six or more carbon atoms. Earlier work, having suggested that polymerization occurred by condensation reactions of acetylene to form linear molecules or diradicals, was concerned over the difficulty of forming cyclic compounds from such species. The formation of products by the radical mechanism removes this difficulty since the addition reaction destroys the sp hybridization and the sp^2 hybridization will give bent radicals. Fourthly, the formation of methane and compounds containing an odd number of carbon atoms may be most easily accounted for by the dissociation of radicals. For example,

$$C_2H_2 + C_2H_3 \rightarrow CH_2{=}CH{-}CH{=}CH$$

$$CH_2{=}CH{-}CH{=}CH \rightarrow CH_3{-}CH{-}C{=}CH$$
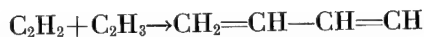
The terminal methyl radical may split off and form methane by abstraction. Similar isomerizations may occur with larger radicals and other radicals containing an odd number of carbon atoms may be formed. Finally, the radical mechanism accounts adequately for the products formed when halogens are added to the reacting acetylene [62].

12. The induction period

As in the reactions of ethylene and propylene the higher molecular weight products are more unstable than the reacting olefin and as these accumulate their dissociation soon contributes appreciably to the reaction. In the reaction of ethylene the rates of formation of the main products formed after the induction period were second order in ethylene and this was interpreted to show that the main initiation both in the initial and in the later stages was the bimolecular reaction of ethylene [44]. The dissociation of the high molecular weight products contributed new products and new propagation steps, but not significantly increased initiation. This is probably the situation in the acetylene pyrolysis, where the kinetics are second order both in the initial stages and in the region of maximum rate. In both regions the main initiation step will be the bimolecular reaction of acetylene to give the vinyl and ethynyl radicals.

13. Reaction of C_2H_2 and D_2

A related reaction with some puzzling features is the H–D exchange in acetylene. Experiments in shock tubes with mixtures of C_2H_2 and C_2D_2 [58] and mixtures of C_2H_2 and D_2 [63] had shown that the isotopic exchange in acetylene was orders of magnitude faster than the conversion to other products. The mechanism suggested, in line with similar studies with other molecules, that exchange occurred through dissociation of a molecular complex between C_2H_2 and D_2. An atomic exchange mechanism for the reaction was proposed by Benson and Haugen [64], but several difficulties with this were pointed out [65], the main ones being the dependence of the rate on the acetylene concentration, the low activation energy and the time required to reach the steady state radical concentration.

A consideration of the mechanism suggested here for the reactions occurring during the pyrolysis of acetylene would lead to the prediction that exchange of H and D in acetylene would occur very rapidly by the addition of atoms to acetylene followed by rapid reversal. Exchange would not require stabilization of the vinyl radical, which would undoubtedly be a third order reaction under shock tube conditions. If initiation occurs by the bimolecular reaction of acetylene instead of by the similar reaction of acetylene and D_2, an atomic exchange mechanism can be written which correctly predicts the observed order of the rate with respect to acetylene and deuterium and the observed activation energy. At 1500 K the former initiation is about six times faster than the latter, for equimolar mixtures.

The main difficulty with an atomic mechanism is that the time required for the steady state concentration of radicals to be attained (about 500 μs) is long compared to the time resolution of the experiments (10 μs), but no induction period was observed. This discrepancy is puzzling but must be resolved before an atomic mechanism could be accepted.

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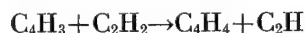
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Discussion

C. F. Cullis (The City University, London):

Dr. Back has included in her paper a very helpful summary of the present situation regarding our understanding of the mechanism of pyrolysis of acetylene. As she is at pains to point out, however, there are a number of questions still unanswered and it is not at present possible, for example, to distinguish between various alternative routes in the radical chain mechanism. Thus, vinylacetylene, which appears to be the primary product of the breakdown of acetylene below ca. 1000 °C, might be formed either by reactions:

$$C_2H + C_2H_2 \rightarrow C_4H_3$$

$$C_4H_3 + C_2H_2 \rightarrow C_4H_4 + C_2H$$

or by reactions:

$$C_2H_3 + C_2H_2 \rightarrow C_4H_5$$

$$C_4H_5 \rightarrow C_4H_4 + H$$
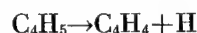
It is probably not going to be possible to determine the extents to which such alternative reaction

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sequences operate simply by means of more detailed studies of the associated overall molecular reactions. Further useful information may, however, be obtained from independent studies of the abstractive and additive reactions of the radicals concerned. Thus, for example, Tarr, Strausz, and Gunning have shown[1] that the reaction

$$C_2H + C_2H_4 \rightarrow C_4H_4 + H$$
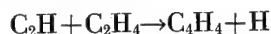
is faster at room temperature than the alternative reaction,

$$C_2H + C_2H_4 \rightarrow C_2H_2 + C_2H_3.$$
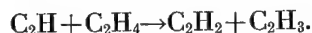
At present therefore, Mr. J. V. Shepherd and Dr. D. J. Hucknall are attempting, at the City University, to study the kinetics of some of the reactions of ethynyl, vinyl and butenynyl radicals, with particular emphasis on their interaction with small alkyne molecules. It is hoped that such studies will throw light on the mechanism not only of the pyrolysis of acetylene and its homologues at relatively low temperatures but also of the formation of carbon at somewhat higher temperatures.

M. H. Back:

I agree with the remarks by Professor Cullis both with respect to the mechanism of formation of vinylacetylene and to the view that measurements of the rate constants for the elementary reactions involved would be very useful. Below about 1000 °C vinylacetylene may indeed arise from reactions of the C_2H or the C_2H_3 radical. The relative importance of each sequence would depend on the relative concentrations of C_2H and C_2H_3 radicals as well as on the rate constants of the reactions involved.

In the mechanism outlined it has been assumed that vinylacetylene is the main primary product of the vinyl radicals while diacetylene is the main primary product of the C_2H radicals. This is an oversimplification which may be partly true but cannot be assessed with confidence until the rate constants for the elementary reactions and heats of formation of the radicals are known more accurately than at present.

R. S. Konar (Catholic University):

I would like to make some comments on the dissociations of ethane and of neopentane.

Ethane Dissociation

The overwhelming experimental evidences [1–5] now show that the high pressure rate constant (k_∞) for the reaction $2CH_3 \rightarrow C_2H_6$ in the gas phase is greater than $10^{13} \exp(-0/RT)$ cm³·m⁻¹s⁻¹, and probably Shepp's number $(k_\infty = 2.20 \times 10^{13}$ cm³·m⁻¹s⁻¹) represents the lower limit for k_∞. Thus in

ethane dissociation,

$$\Delta S_{298\,K} \qquad \Delta H_{298\,K} \text{ (kcal m}^{-1}\text{)}$$

$$C_2H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2CH_3$$

$$37.1(\pm 1.0), \qquad 88.20(\pm 3.0)$$
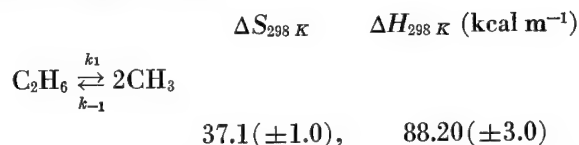
[where the entropy (S) is in cal·deg⁻¹ mole⁻¹. Standard state ideal gas at 1 atmos; thermochemical data are taken from Benson [6], and Purnell and Quinn [7]].

$$k_1 = 10^{17.08} \exp(-87600/RT) \text{ s}^{-1}$$

if $k_{-1} = 10^{13.30} \exp(-0/RT)$ cm³·m⁻¹·s⁻¹.

By measuring the initial rate of CH_4 formation, Quinn [8] found

$$k_1 = 10^{17.45} \exp(-91700/RT) \text{ s}^{-1},$$

while Lin and Back [9] first found

$$k_1 = 10^{16.0} \exp(-86000/RT) \text{ s}^{-1},$$

and later on

$$k_1 = 10^{16.45} \exp(-88000/RT) \text{ s}^{-1}.$$

(see Lethard and Purnell [10] for a discussion). It is suggested here that these discrepancies are probably due to the differences in the experimental approach to the problem.

Quinn measured methane by taking samples directly from the reaction vessel, and injecting it into the G.C. (integrated with the reaction system via an automatic gas sampling valve). He measured the initial rate of CH_4 formation before the secondary reactions started in the system (fig. 2 of reference 8). The Arrhenius parameters as reported by Quinn are somewhat higher than the average values as shown above, and this may well be partly due to the error in the absolute calibration of CH_4 in the G.C. columns.

Lin and Back [9] measured CH_4 indirectly, i.e. they froze all the products and the unreacted reactant at the liquid N_2 temperature, and then toeplered the noncondensables. It is found that under such conditions, all CH_4 is not collected in the toepler pump although in principle it should be collected by the pump. The situation gets worse if there is hydrocarbon or inert gas matrix which retains a considerable amount of CH_4 by trapping. H_2 and CH_4 were then analyzed by combustion of hydrogen in a copper oxide furnace maintained at 280 °C (for details see page 506 of reference 9). It may well be that Lin and Back did not collect all the CH_4, and as a consequence might have underestimated the initial rate of CH_4 formation. This is reflected in the low value of A_1.

The initiation reaction in ethane dissociation can also be studied by measuring the initial rates of n-butane and of ethyl formations coming from the reactions (5a) and (5b) (see page M0). Lin and Back did find that at high pressures,

$$d(n-C_4H_{10})/dt = k(C_2H_6)$$

[1] A. M. Tarr, O. P. Strausz, and H. E. Gunning. Trans. Faraday Soc. (1966) 62, 1221.

where $k = A \exp(-89800/RT)$ s^{-1}, and $n-C_4H_{10}$ was measured by L. E. Reid and D. J. LeRoy [11] have measured (k_d/k_c) of ethyl radicals, which is given by:

$$\log_{10}(k_d/k_c) = -0.213 \pm 0.014 - (906 \pm 30)/(2.3RT)$$

Hence $E_1 = 90.7$ kcal/mole. Thus,

$$k_1 = 10^{16.5} \exp(-88000/RT) \text{ s}^{-1}$$

$$= A_1 \exp(-90700/RT) \text{ s}^{-1}.$$

Hence $A_1 = 10^{17.30}$ s^{-1}. It is interesting to note that O'Neal and Benson [12] estimated

$$k_1 = 10^{16.75} \exp(-89500/RT) \text{ s}^{-1},$$

assuming

$$k_{-1} = 10^{12.9} \text{ cm}^3 \cdot \text{m}^{-1} \cdot \text{s}^{-1}$$

for which the experimental evidence is very poor. It is clear that because of analytical errors, one can hardly expect the expected Arrhenius parameters from such complex pyrolytic reactions. Thus from the experimental standpoints, the best Arrhenius parameters for k_1 are $k_1 = 10^{17.30} \exp(-90700/RT)$ s^{-1}.

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Neopentane

By measuring the initial rate of C_2H_6 in neopentane pyrolysis, Halstead et al. [1] found k_1 as

$$k_1 = 10^{18.05} \exp(-85800/RT) \text{ s}^{-1}$$

$$(CH_3)_4C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (CH_3)_3C + CH_3$$
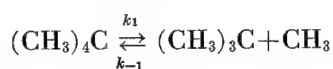
The estimated endothermicity of [1] at 298 K is (80.4 ± 3.0) kcal mole^{-1}, if ΔH_f^0 of $(CH_3)_3C$ radical at 298 K is 6.7 ± 1.0 kcal mole^{-1}, and is (82.5 ± 3.0) kcal·mole^{-1} if the ΔH_f^0 of the $(CH_3)_3C$ radical is (9.1 ± 1.0) kcal mole^{-1} as reported by Tsang.[2]

If we want to correlate the estimated endothermicity (ΔH_T) with the activation energy of the process (E_1), it is necessary to know the value of E_{-1}, since

$$\Delta H_T - \Delta nRT = E_1 - E_{-1}.$$

Some kineticists believe that E_{-1} is zero, some think E_{-1} is a positive quantity, while others suggest that E_{-1} is a negative quantity [2]. However all gas kineticists accept that the experimentally measured (k_d/k_c) ratio of alkyl radicals given below is probably correct.

$2C_2H_5$, $(CH_3+C_2H_5)$, $(CH_3+n-C_3H_7)$,

$$(CH_3+i-C_3H_7), \quad (CH_3+t-C_4H_9),$$
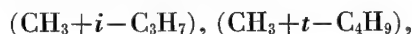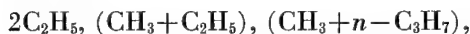
| $\dfrac{k_d}{k_{c298\,K}}$ | 0.13, | 0.36, | 0.058 | 0.163 | 0.70 |

and that for two ter-C_4H_9 is 2.30, (Terry and Futrell [3], Trotman-Dickenson and Milne [4]).

If E_{-1} is zero, then it is very hard to explain all these experimental data. The E_c for the two ethyl recombination has been measured by Shepp and Kutsche [5] as 2.0 kcal mole^{-1}, while (k_d/k_c) by Reid and LeRoy [6],

$$\log_{10}(k_d/k_c) = -0.213 - 906/(2.3RT),$$

i.e., E_d for the two ethyl is about 3.0 kcal/mole, (see also Ivin and Steacie [7]). Comparing the (k_d/k_c) of two ethyl radicals and of $(CH_3+ter-C_4H_9)$, I am inclined to think that E_c (i.e. E_{-1}) of $(CH_3+ter-C_4H_9)$ cannot be zero, and must be greater than the E_c of two ethyls. Thus E_{-1} may be as high as 3 to 4 kcal mole^{-1} due to steric barriers [8]. On this basis the measured $E_1 = 85.8$ kcal/mole is not inconsistent with the estimated endothermicity of the process [1], which is certainly not better than ± 3.0 kcal/mole.

Tsang [2] has himself questioned his own shock tube results. He believes that he might have studied the reaction (1) in the slightly pressure dependent region, and there may well be a molecular process such as

$$(CH_3)_4C \rightarrow iso\text{-}C_4H_8 + CH_4$$

under his experimental conditions [2]. In that case, the measurement of total isobutene would not give k_1.

Taylor et al. [11] studied neopentane pyrolysis in a flow reactor, and from the product analysis estimated the overall rate of neopentane disappearance. They found experimentally that at or above 1 percent conversion,

$$-d(C_5H_{12})/dt = k(C_5H_{12})$$

where $k = 10^{16.9} \exp(-80500/RT)$ s^{-1}. They then assumed that k must be k_1, since the overall order is unity, and the overall activation energy is very close to the estimated endothermicity of the process (1) at 298 K.

From the analytical data of Taylor et al, it is clear that they have studied the isobutene inhibited decomposition of neopentane, and not neopentane

itself. The overall order (unity) and overall low activation energy (80.5 kcal/mole) may well be the consequence of self-inhibition (see ref. 1).

Taylor et al. did not produce any data below 1 percent conversion and the extrapolation of $-$log (percent conversion) versus time to zero time would not give the correct rate constant, and hence the initial rate, in the inhibited decompositions if the conversion is high (1 percent or above). The presence of olefins masks the normal reactions [1, 14]. It has been found experimentally that when neopentane is pyrolysed at 500 °C with 1 percent isobutene, CH_4 is formed at a constant rate initially and the pressure-time curve when extrapolated goes through the origin; but it does not give the kinetics of neopentane pyrolysis. In the absence of olefins (added), CH_4 rate decreases with time [1]. This is also the case in the flow reactor of Taylor et al. (fig. 4, ref. 11). They have claimed that they have studied the homogeneous reaction, but did not measure H_2, a major product, nor did show its distribution inside the reactor. It appears H atoms will reach the reactor wall under their experimental conditions. It was found that neopentane diffused to the wall in about 0.3 secs. and the time of residence was up to 0.4 secs. Thus there is considerable doubt about the validity of the measurement of k_1 by the method of Taylor et al., and so their results have to be accepted with considerable reservation.

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M. H. Back:

Dr. Konar has provided arguments in support of the rate constant reported by Quinn for the elementary dissociation of ethane. The frequency factor measured by Quinn was in good agreement with the rate constant for the reverse combination of methyl radicals but the activation energy for the dissociation

which he measured gave a heat of formation of the methyl radical of 35.6 kcal/mole at 298 K, which in turn leads to a dissociation energy of methane of 105.6 kcal/mole. This value is probably too high and it appears not possible to find agreement among the four quantities k_1, k_{-1}, ΔS and ΔH for the system

$$C_2H_6 \overset{1}{\underset{-1}{\rightleftarrows}} 2CH_3$$
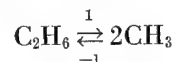
Regarding the measurements of the rate constant for the dissociation of neopentane, Dr. Konar's caution in accepting measurements at conversions greater than 1 percent may be well-founded. Indeed very low conversions were needed in the work done in the static system. The data reported by Taylor et al. from the experiments in the flow reactor shows, however, that they were measuring initial rates of formation of methane, although the accuracy did not appear very good. Perhaps it is simply a combination of errors which leads to the low value of 80.5 kcal/mole for the dissociation of neopentane. Their work was discussed in relation to the previous measurements on neopentane by Baronnet and Niclause (ref. 4 of the discussion).

A. S. Gordon (Naval Weapons Center):

Referring to the mechanism of ethene pyrolysis, I would be interested in any experimental evidence that a vinyl radical (or a homologue) will disproportionate with about zero energy of activation. My interest is aroused because an internal hydrogen transfer reaction,
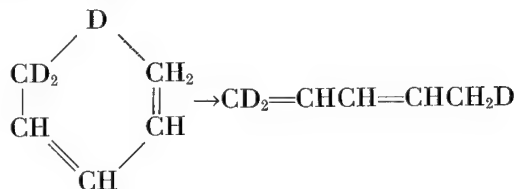
has $\Delta H = 0$, but an $E_{act} \simeq 35$ kcal/mole. This reaction bears some formal relation to the hydrogen transfer reaction between two ethylenes. In addition, endothermic abstraction reactions, e.g. allyl radical abstracting from a saturated hydrocarbon, have a barrier in addition to the endothermicity of the reaction. The two types of reactions suggest that the H transfer reaction between two ethylenes might have a larger barrier than the endothermicity.

M. H. Back:

There is to my knowledge no direct evidence that disproportionation between a vinyl and an ethyl radical occurs without activation energy. This assumption was made on the basis of what is known about the rates of radical-radical combination and disproportionation reactions involving small hydrocarbon radicals. Almost all the evidence leads to the conclusion that disproportionation reactions between such radicals require no activation energy. In view of the considerable exothermicity of these reactions

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this result is not surprising. The reactions discussed by Dr. Gordon, on the other hand, are hydrogen transfer reactions which often, as he points out, have heats of reaction close to zero and which may involve a considerable activation energy. Now two important differences between these types of reactions could lead to considerable differences in the activation energies involved. (1) Disproportionation reactions are highly exothermic while abstraction reactions may be close to thermal neutral. For example,

$$2C_2H_5 \rightarrow C_2H_4 + C_2H_6$$

$$\Delta H = 59 \text{ kcal/mole}$$

$$C_2H_3 + C_2H_5 \rightarrow 2C_2H_4$$

$$\Delta H = 65 \text{ kcal/mole}$$

$$CH_3 + C_4H_{10} \rightarrow CH_4 + C_4H_9$$

$$\Delta H = 5.3 \text{ kcal/mole}$$

$$CD_3CH{=}CHCH{=}CH_2 \rightarrow CD_2{=}CHCH{=}CHCH_2D$$

$$\Delta H = 0$$

(2) The dissociation energy of the C–H bond broken is very different in the two cases. In the disproportionation reaction the C–H bond dissociation energy is probably reduced to about 40 kcal/mole, while the C–H bond broken in the abstraction process very likely has close to its normal strength of about 100 kcal/mole.

Dr. Gordon's second point is that an endothermic reaction involving radicals may require an activation energy considerably greater than the endothermicity. This of course depends entirely on the nature of the reverse reaction and in the case of our proposed initiation reaction in the ethylene system

$$2C_2H_4 \rightarrow C_2H_5 + C_2H_3$$

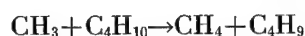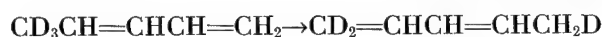we equate the activation energy for this reaction to the endothermicity by assuming that the disproportionation between a vinyl and an ethyl radical has the same energy requirements as the disproportionation between two ethyl radicals.

W. Tsang (National Bureau of Standards):

The mechanism, rate constants, and parameters of the initial step in the gas phase pyrolysis of most organic molecules can be conveniently and accurately determined using the comparative rate single pulse shock tube technique[1]. This is because the shock tube has all the characteristics of an ideal pyrolytic reactor. Wall reactions are eliminated and the short reaction time (1 μs) excludes the possibility of chain decomposition. Using this technique rate parameters for the initial step in the decomposition of over 50 hydrocarbons (up to C_{12}) have been determined. With respect to the alkanes they show striking regularities. There are no molecular modes of

reaction. All variations in rates are due to activation energy changes. They are generally in good agreement with presently accepted[2] values of bond energies. The preexponential factor per C–C bond being ruptured appears to be a constant with the appropriate number being 2×10^{16} s^{-1}. Calculated preexponential factors from measured radical recombination rates in the literature are however a factor of 10 to 30 higher. This is the same phenomena as observed by Professor Back.

The shock tube technique is applicable to the study of the pyrolysis of any compound with a vapor pressure of about 10 μm or above. For really large hydrocarbons a heated shock tube is necessary. This is not a problem. On the other hand from the general trends already observed, startlingly new behavior should not be expected.

From the data on ethane as summarized by Professor Back it appears that for such simple systems the classical static technique may give acceptable rate constants, they do not yield dependable rate parameters. Thus any set of rate parameters derived from a given static experiment must be regarded with extreme caution.

M. H. Back:

Any one set of rate parameters from a given experiment, whether by static, flow or shock tube technique, must always be regarded with caution. The rate parameters for the dissociation of ethane which I have discussed were obtained from several sets of experiments and indeed the parameters obtained from the static technique were in good agreement with those obtained by Dr. Tsang from his experiments in shock tubes. The data from both techniques show a discrepancy with the radical recombination rates and it is this discrepancy which I wished to call attention to in my discussion. The reasons for it are not yet fully understood.

A. S. Gordon and R. H. Knipe:

We believe that the saturated hydrocarbons (alkanes) have been shown to decompose exclusively via a chain mechanism even previous to the work of Tsang. However, there are other classes of hydrocarbons which do decompose exclusively via a molecular process (or biradical which reacts so fast that it is indistinguishable) as discussed in our paper.

As for Dr. Tsang's technique: while it is mostly free of wall, Kistiakowsky and his students have shown that small quantities of gases are desorbed from the walls of shock tubes and influence the reaction. Also, the shaping of the pulse to give a step rise to a given temperature and a similar decrease at the end of pulse leaves some error in the results. The most important criticism of his technique is that he must rely on toluene (or some similar agent) to completely quench the free radicals. When acting in this manner the benzyl radical is assumed not to

[1] W. Tsang, J. Chem. Phys. **43**, 352 (1965); **44**, 4283 (1966); **46**, 2187 (1967). Int. J. Chem. Kinetics **1**, 245 (1969).

[2] J. A. Kerr, Chem. Rev. **66**, 465 (1966).

abstract hydrogen from the parent compound. The assumption is not correct; it will abstract with an activation energy greater than the alkyl radical because of its resonance energy. The higher the temperature of the reaction the less effective the technique. Actually, the technique is not restricted to the shock tube but has been applied in static and flow systems, where it was pioneered by M. Szwarc.

The single pulse shock tube has the advantage that it can reach higher temperatures than the classical techniques. In using the technique at higher temperatures it must be carefully established whether the hydrocarbon is in its "fall-off" region. For the lower temperature region, the classical techniques of a static system where it can be experimentally established that the reaction is homogeneous, allow the various parameters such as pressure, inert gases, and temperature to be more conveniently explored than in a shock tube. As is so often the case, no one experimental or analytical technique can be used to solve the research problem area.

W. Tsang:

Drs. Gordon and Knipe have made the common assumption that the only special attributes of shock tube studies are high temperature and relative homogeneity of reactions. They have failed to draw the proper consequences that arise from the short reaction time ($\sim$1 ms) and low reactant concentrations ($\sim$.01 percent in argon or 3×10^{-6} moles/liter under experimental conditions). More than anything else these isolate the initial processes for study. Consider, for example, a methyl radical in this environment; the rate expression for its abstraction reaction with a typical hydrocarbon (say n-butane) as recommended by A. F. Trotman-Dickenson and G. S. Milne [Table of Biomolecular Gas Reactions, NSRDS-NBS 9, U.S. Government Printing Office] is

$$k(CH_3 + nC_4H_{10} \rightarrow CH_4 + C_4H_9)$$
$$= 10^{8.0} \exp(-7,600)/RTl/\text{mole s.}$$

At 1100 K (the usual shock tube temperature) this is $10^{6.5}$ l/mole s. With a hydrocarbon concentration of 3×10^{-6} moles/liter this is equivalent to a methyl radical lifetime (with respect to abstraction) of 0.1 s. Remembering that the total reaction time is only 0.001 s, this means that methyl radicals are stable under shock tube conditions. Since there is no question that the comparable benzyl radical reaction must be even slower, it is clear that the suggestion by Drs. Gordon and Knipe is not applicable to these shock tube studies.

Note that it may be (and has been) used in explaining the serious errors in the original toluene carrier work of Szwarc. These are carried out with much higher concentrations and longer residence times. More complete discussions of this and the other minor points may be found in our publications [W. Tsang, Internat. J. of Chemical Kinetics 2, 311 (1970) and references therein].

It should be noted that the basic correctness of the rate constants determined by the single pulse shock

tube studies have now been verified by flow [J. E. Taylor, D. A. Hutchings, and K. J. French, J. Amer. Chem. Soc. **91**, 2215 (1969)]; static [M. P. Halstead, R. Martin, D. A. Leathard, R. M. Marshall, and J. H. Purnell, Proc. Roy. Soc. Ser. **A. 310**, 525 (1969)]; and very low pressure pyrolysis studies [N. Spokes, personal communication].

Leo A. Wall (National Bureau of Standards):

Drs. Gordon and Back have given very excellent discussions of thermal decomposition reactions; however, they confined their remarks to very small molecules. I would like to turn their attention to large molecules, for example alkanes with ten or more carbon atoms, and ask them to comment on the following:

F. O. Rice discussed the thermal decomposition of large alkane molecules many years ago (The Aliphatic Free Radicals, Rice and Rice, The Johns Hopkins Press, 1935) and later the isomerization of large free radicals (A. Kossiakoff and F. O. Rice, J. Am. Chem. Soc. 65: 590 (1943)) was invoked to improve the fit of the original free radical theory with experiment. A premise of the free radical theory was that large radicals were unstable and decomposed to small ones. It has occurred to me that actually large radicals are quite stable and in a sense inert. In the polymer field the conformation of molecules is very important. In molecules containing ten to forty or more carbon atoms, one would suspect that conformation would play an important role in gas pyrolysis. In a twenty or so carbon atom molecule an active radical end could be shielded or in effect buried and not easily reacted with other molecules, hence, except for isomerization, decomposition to smaller species would be the only course they could follow.

M. H. Back:

The reactivity of radicals in an energetic sense does not appear to change very much after about C_5 or C_6, at least for straight chain radicals. Long chains are remote from the reactive part of the radical and will have very little effect on the energetics of the radical reaction. Dr. Wall has suggested that there may be other important influences besides energy requirements on the rates of reactions of long chain polymer radicals, for example, conformational effects. The reactive end of a radical may become shielded or buried and bimolecular reactions might be hindered relative to unimolecular reactions. The effect would be manifested in the entropy of activation of the transfer process, while the energy of activation would show little change. The entropy term in the thermodynamics of the polymerization process is responsible for the observation of a ceiling temperature for the reaction. A large entropy term arising from conformational effects on the reactions of the polymer radical would thus have an effect on the ceiling temperature. A comparison of ceiling temperatures for various types of polymerizations

might give some indication of the importance of conformational effects.

A. S. Gordon and R. H. Knipe:

We agree with Dr. Wall that a large hydrocarbon radical would be less likely to stabilize itself by H abstraction from another molecule or radical than a small radical. Since the unimolecular isomerization reactions are probably the fastest reaction paths in the gas phase, it is likely that the various isomers of a large radical would tend to be present in their equilibrium proportions. In the case of the large radical many of the isomers would have the free radical end buried inside the coils of the structure, so that these would not be able to abstract H from other molecules. In a practical situation large radicals could exist in the gas phase only in very low concentrations except at high temperatures because of vapor pressure limitations. At high temperatures the unimolecular cracking reactions would be very fast.

Factors Involved in the Degradation of Polymers in Melts

C. R. Patrick

The Department of Chemistry, University of Birmingham, Birmingham, England

The full interpretation of degradation of molten polymer would be facilitated by a better understanding of the elementary chemical processes involved. Suitable analogues of these reactions may often be studied in detail only in the gas phase. Relationships between the kinetics of elementary reactions in gas and liquid phases are desirable. On the basis of thermodynamic arguments it is concluded that Arrhenius parameters for bimolecular reactions in the two phases should differ, to a small but significant extent, greater than usually accepted, whilst those for unimolecular processes, commonly should not. Diffusion may determine the rates of some reactions in liquids particularly of reactions between radicals. Evidence on the mobilities of large and small molecules, models for radicals, in molten polymers, is summarized. Expressions for diffusion controlled reactions are compared, and applied to reactions in molten polymers. Complicating effects in the size dependence of the rates of diffusion controlled reactions between macroradicals are surveyed. Other complicating effects, notably of geminate reactions between radicals, are discussed. A case is made out for comparing more extensively the kinetics of thermal degradation of gaseous paraffins, and of molten paraffins and polyethylenes.

Key words: Degradation of polymers in melts; diffusion-controlled reactions between macroradicals; diffusivities of molecules and radicals in molten polymers; geminate recombination of radicals; pyrolysis of hydrocarbons; rates of reaction in liquids and gases; reaction equilibria in liquids and gases.

1. Introduction

This paper examines the bases upon which kinetic parameters, which for simple substances may be characterized in the gas phase, may be related to kinetic parameters for the same, or similar, processes in the liquid phase. The comparison is made on a thermodynamic basis. It is also necessary to acknowledge that the rates of some reactions in liquids, such as those involving free radicals that are of importance in the chain degradation of addition polymers, are regulated by diffusion, rather than by chemical factors. Such diffusion-controlled reactions will be discussed, and outstanding problems will be indicated.

2. Thermodynamic Considerations of Reactions in the Gas and Liquid Phases

We will consider the thermodynamics for the equilibrium between a set of reactants and products, and their relation to the thermodynamics for the same equilibrium in the liquid phase. We assume that the components form thermodynamically ideal mixtures in both phases. Equilibrium constants for reactions in the gas phase are generally formulated in terms of the partial pressures of the reactants and products, using reference states of one atmosphere pressure for the respective substances. Equilibrium constants in the liquid phase are most appropriately formulated in terms of the mole fractions of the

components, that is, with reference to the (real or hypothetical) pure liquids (strictly at a defined pressure, which, for the present purposes, will be assumed to be a low pressure—say one atmosphere). The heats of reaction in the gas and liquid phases ($\Delta H_{R,g}$ and $\Delta H_{R,l}$, respectively) are related by the heats of vaporisation (ΔH_v) of the component liquids in their reference states to the reference states of the gases ($P = 1$ atm). Thus:

$$\Delta H_{R,g} - \Delta H_{R,l} = \sum_{products} \Delta H_v - \sum_{reactants} \Delta H_v$$

Similarly the standard entropies of reaction are related by

$$\Delta S_{R,g} - \Delta S_{R,l} = \sum_{products} \Delta S_v - \sum_{reactants} \Delta S_v$$

where the entropies of vaporisation, ΔS_v, relate to changes of state specified for the heats of vaporisation. The first of these relationships has often been presented [1, 2, 3, 4][1] but the second has not been exploited fully. The detailed development of these equations cannot be pursued in this paper. At temperatures below, and remote from, the critical temperatures of the liquids, the appropriate heats and entropies of vaporisation are, in principle, easily determined. In the neighbourhood of the critical temperature the quantities required are not easily obtained, and the major contributions to them are due to the non-ideality of the vapors, rather than to

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[1] Figures in brackets indicate the literature references at the end of this paper.

the vaporisation of the liquids. Above the critical temperatures of the liquids formally identical relationships still obtain, but the terms for the vaporisation of the substances need strictly to be redefined. The solution of a gas in a solvent with which it has no strong interaction is not accompanied by a change in heat that is comparable in magnitude with the heat of vaporisation of the same substance as a liquid [5]. There is, however, a significant change in entropy when a gas is dissolved (at constant pressure) in a liquid, and this, when extrapolated to the limit at which the liquid is composed of the hypothetic liquified gas, is very similar in magnitude to that for the vaporisation of a normal liquid to the vapour at the same pressure and temperature (that is about 22 cal·deg^{-1} mole^{-1} for vaporisation to $P=1$ atm at 25°). This result was embodied in earlier work [5] but was only recently made explicit [6]. It is easily understood. In the gas the motions of the molecules are limited only by the total volume of the system. In the liquid, motions are confined to a very small volume, commonly referred to as the free volume. The change in entropy on this account is similar for all molecules, because, in simple terms it is only the change in volume available for the molecular motion that matters.

Some generalisations follow from these relationships. In equilibria that involve no change in molecularity, it is likely that the summed heats of vaporisation will equal very nearly those of the products, so that $\Delta H_{R,g} - \Delta H_{R,1}$ will be small. In associative equilibria, of the type $A+B \rightleftharpoons AB$, [7] the disparity between the sums of heats of vaporisation of reactants and products is likely to be greater, so that, unless some of the species are, at the temperature of interest, real gases, $\Delta H_{R,g} - \Delta H_{R,1}$ will commonly be significant and negative.

Troutons rule [7, 8] teaches that the entropies of vaporisation of many substances are approximately equal at all temperatures, and are about 21 cal deg^{-1} mole^{-1}. Thus for equilibria involving no change in molecularity, $\Delta S_{R,g} - \Delta S_{R,1}$ should be small, and in associative equilibria, as defined above, $\Delta S_{R,g} - \Delta S_{R,1}$ should generally be about -21 cal deg^{-1} mole^{-1}.

The predictions relating to equilibria involving no change in molecularity are demonstrated by measurements on equilibria between halogens and diatomic interhalogen compounds [2, 9]. Predictions for associative equilibria are less well illustrated. The entropies of dimerisation of carboxylic acids in the gas phase ($-$ (34 to 36) cal deg^{-1} mole^{-1}) are greater than those in solution ($-$ (10 to 14) cal deg^{-1} mole^{-1}) [10], and the differences are about $-$(20–23) cal deg^{-1} mole^{-1}) as expected. The heats of dimerisation in the gas phase ($-$ (14 to 16) kcal mole^{-1}) are greater than those in the liquid phases ($-$ (8 to 10) kcal mole^{-1}) [10]. These results accord with our simple theory, and do not imply, as has been suggested [10] that the reactants interact in a special way with the solvents used. Direct experimental evidence to test our predictions for associative equilibria are sparse. With one notable exception, the dimerisation of nitrogen dioxide [11] the predictions are, however, supported reasonably well by a body of evidence, too extensive to review here, but which deserves further assessment.

3. Application of Thermodynamic Results to Reaction Kinetics

Reaction rate coefficients are conventionally defined in terms of concentrations and changes in concentration. For any chemical process (for example $A+B \rightleftharpoons AB$) we may define rate coefficients k_f and k_r for the forward and reverse reactions respectively. These are related to the equilibrium constant for the reaction, expressed in terms of concentrations: $K_c = k_f/k_r$ [12]. We continue to consider thermodynamically ideal systems. More generally the relationship between rate coefficients and equilibrium constant still obtains at equilibrium, but the rate coefficients, since they have been defined in terms of concentrations, rather than activities, may vary with concentration. Considering further reactions in liquids, in which the thermodynamic equilibrium constant K_x is defined in terms of mole fractions [12] we have

$$K_x = K_c V_s^{\Delta n}$$

where Δn is the difference between the number of molecules of products and the number of molecules of reactants in the stoicheiometric equation for the reaction, and V_s is the volume of liquid that contains one mole of substance. We may write:

$$K_x = \exp[\Delta S_{R,1}] \cdot \exp[-\Delta H_{R,1}/RT]$$

and

$$K_c = B_c \exp[-\Delta H_{R,1(c)}/RT]$$

To a commonly adequate approximation [13]

$$\Delta H_{R,1} = \Delta H_{R,1(c)} \quad \text{and} \quad B_c = V_s^{-\Delta n} \exp[\Delta S_{R,1}/R]$$

The preexponential factors, A_f and A_r, for the forward and reverse rate coefficients, are related by $B_c = A_f/A_r$, and the corresponding energies of activation are related by $\Delta H_{R,1(c)} = (E_r - E_f)$.

Taken together with the conclusions of the previous section these equations offer the possibility of making predictions about, and testing the consistency of, rate coefficients in liquids, particularly since it is possible, with reasonable confidence, to predict the entropies of reactions in the gas phase [14].

Standard entropy changes for associative reactions ($A+B \rightarrow AB$) in the gas phase lie in the approximate range $-$(37 to 48) cal deg^{-1} mole^{-1}, so that those in the liquid phase might be expected to lie in the range $-$(15 to 28) cal deg^{-1} mole^{-1}. In a solvent composed of small molecules, V_s is about 0.1 l mole^{-1}, so that B_c is about $10^{-6\pm1}$ l mole^{-1}. In a polymeric matrix, having an average molecular weight of 5×10^4, V_s may be 50 l mole^{-1}, so that B_c is about $10^{-4\pm1}$ l mole^{-1}.

4. Comments on Rate Coefficients in Gas and Liquid Phases

Equilibrium constants for unimolecular isomerisations should be nearly equal in the two phases, so that the rate coefficients must be nearly equal, or change by approximately equal factors in passing from one phase to the other. Since for associative reactions the equilibrium constants differ for the two phases, either or both the rate coefficients involved must change in passing from one phase to the other. Arguments based upon the transition state theory of reaction rates, and a weak argument based upon the likely behaviour of rate coefficients in unimolecular isomerisations, suggest that the Arrhenius parameters for rate coefficients in the gas and liquid phases may differ significantly for bimolecular processes, but less so, or only very slightly, for unimolecular reactions (saving those influenced by diffusion). Other authors [2, 15, 16] have reached similar conclusions using detailed treatments of rate coefficients, but have made approximations which, whilst they might appear plausible are not strictly thermodynamically consistent. Kinetic results, which are very sparse, particularly for bimolecular reactions, do not support the predictions. Data most frequently cited for bimolecular reactions in this context [17], namely those for the dimerisation of cyclopentadiene, are not thermodynamically consistent.

For illustration we apply our principles to the decomposition of t-butyl peroxide. The rate coefficient for the decomposition in solution is $3 \times 10^{14} \exp[-35,000/RT] \mathrm{s}^{-1}$ [18]. (In this and subsequent like expressions R is in cal deg^{-1} mole^{-1}). The rate coefficient for the association of t-butoxy-radicals in solution is $1.8 \times 10^8 \exp[\pm 2,000/RT]$ l mole^{-1}s^{-1} [19], say about $10^{8 \pm 1}$ l mole^{-1}s^{-1}. Thus B_c is about $10^{-6 \pm 1}$ l mole^{-1}. The standard entropy change for reaction in the gas phase is about -40 cal deg^{-1} mole^{-1} [20]. The entropy change in the liquid, therefore, should be about -20 cal deg^{-1} mole^{-1}. The discrepancy is disappointing, but it should be remembered that rate coefficients, and more especially their Arrhenius parameter, are often subject to greater errors than are admitted. The preexponential factor for the gas phase decomposition of t-butyl peroxide is close to 10^{16}, s^{-1} greater than that in solution, whilst the energy of activation (about 38 kcal/mole) is also greater than that quoted for solution [21]. On the other hand the rate coefficients for the recombination of the radicals appear to be very similar in the two phases (ca. 10^8 l mole^{-1} s^{-1}) [19, 21]. The example has been chosen to illustrate difficulties—either in the uncertainties in the experimental data, or in the evaluation of the theory.

5. The Effects of Non-Ideality of Thermodynamic Behaviour

Thermodynamically ideal behaviour is rare in liquid mixtures. The standard entropy of vaporisation will differ in nonideal solutions, but must commonly remain of the same order, except where the non-ideality results from very strong interactions which may be regarded as chemical in nature. Our arguments, saving such exceptions, must provide useful, if sometimes poor, approximations for non-ideal solutions. It is interesting to speculate on whether free radicals will form markedly non-ideal solutions.

6. The Possible Effects of Diffusion on the Rates of Thermal Degradation of Polymers

Diffusion of reactants and products within polymer melts may effect the rate of degradation in two principal ways. Firstly, some products of reaction may diffuse so slowly out of the system that they interfere with the main course of the reaction. This was noted in the degradation of polymethylmethacrylate, where the major product, monomer, remained in the polymer in sufficient concentrations to cause a back-reaction [22]. The detailed analysis of such a situation has been given [23]. Secondly the rates of reaction together of free radicals may be determined by rates of diffusion as in polymerising systems [26, 15, 64] and decomposition of polymers in solution [25].

7. Diffusivities of Molten Polymers

In view of the difficulties involved it is not surprising that few measurements have been reported of diffusivities in polymers at high temperatures particularly in the range (200–450°) where thermal degradation is important. It is necessary, therefore, to estimate values using theoretical or semiempirical relationships. We shall consider the behaviour of two extreme classes of molecules, namely of macromolecules, comparable in size with those which compose the greater part of the mass of polymer, and small molecules, comparable in size with monomeric units, or other small products of decomposition.

The viscosities of polymer melts are more easily measured than are the diffusivities of the constitutent molecules. It is convenient, therefore, to use the relationship between the viscosity, η, and the self-diffusivity, D, of the system of macromolecules: [24, 27].

$$D\eta = A(T) = (\rho N_{\mathrm{Av}}/36)(R^2/M)kT$$

where R^2 is the mean square end-to-end distance of the polymer chain, M is the molecular weight, ρ is the density, and N_{Av} is Avogadro's number. The validity of the relationship has been demonstrated, but chiefly for bulk or swollen polymers at temperatures of up to about 50° above their glass transition temperatures [28]. The greatest dependence of $A(T)$ upon T is through the term kT.

The term (R^2/M) is not very sensitive to temperature, or to changes in molecular weight. Although it depends upon the structure of the repeating unit it is not very markedly so. Experimental values of A

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are about $(4-8) \times 10^{-8}$ cm^2 at about 50° [28]. The equation was derived for, and is best understood if applied to, systems composed of polymers of uniform molecular weight. Most real systems contain a wide range of molecular weight, so that the value of D to be associated with η in the above equation has no simple significance.

Viscosities of melts have not always been measured for the molecular weights or temperatures in which one is interested. In order to estimate the required properties the following relationships may be used:

$$\log \eta = 3.5 \log M + \text{constant} \qquad [30, 29]$$

$$\log \eta = -8.86(T - T_s)/(101.6 + T - T_s)$$

$$[24, 27, 31, 32]$$

where $T_s = (T_g + 50)$, and T_g is the glass transition temperature of the polymer. The second relationship holds only for molecular weights greater than a certain value, characteristic of the polymer, but generally about 10^3–10^4 [33]. For polymers of lower molecular weight, which do not entangle with one another to such great effect, η is approximately proportional to M [34, 35, 27]. (There is some evidence that at very high molecular weights ($>10^6$) η varies more rapidly with M than $M^{3.5}$ [36]. M may be an average (weight-average) molecular weight [27, 32].

The temperature-dependence of viscosities of melts, following the expression quoted, does not approach the Arrhenius form except at high temperatures [27]. The limiting approximately Arrhenius form indicated by the expression requires an energy of activation that is independent of molecular constitution and is about 4 kcal/mole [32]. This is not true of liquids in general [32]. The equation may not apply at high temperatures. An alternative expression has been suggested but not justified for extrapolation to temperatures far in excess of $(T_g + 100)$ [30].

A significant implication of these equations is that the temperature-dependences of η and D are independent of molecular weight, at least to a good approximation. The constants of proportionality in these expressions vary considerably from one polymer to another, so that interpolations of data between different polymers is inadvisable [30].

Amongst polymers whose thermal degradation has been of interest, polytetrafluoroethylene (PTFE) is notable in possessing a very high melt-viscosity [37], which is in the region of 10^{11} poise, in the temperature range 330–390 °C. The polymer is generally of high molecular weight ($>10^7$). The viscous relaxation of PTFE melts at 380°, having M in the range 10^5–10^8, shows a dependence on $M^{0.8}$ rather than $M^{3.5}$ [38]. If, as is questionable in view of the latter observations, we may assume $D\eta = A(T)$ and use a typical value for $A(T)$ (say 10×10^{-8} cm^2) we estimate that in the PTFE melts described, the effective self-diffusivities lie between 10^{-17} and 10^{-19} cm^2 s^{-1} [39]. The apparent energy of activation for viscous flow in this temperature region is 36 kcal/mole [37], although it has been suggested the

energy of activation varies over the temperature range [40]. Over the range of temperature of interest for the thermal degradation of the polymer (380–450 °C) [23], the diffusivity is likely to vary by a factor of less than 15.

The diffusivity of radioactively labelled polystyrene ($M = 8 \times 10^4$) in polystyrene of higher molecular weight ($10^5 \times 10^6$) at 237 °C is 1×10^{-10} cm^2 s^{-1} [41] and independent of molecular weight of the substrate [42]. Whilst these results do not prove the point, they are consistent with the view that, provided M is large, diffusivities of macromolecules are proportional to $M^{-3.5}$ independently of the composition of the matrix. M is here the molecular weight of the diffusing polymer, and not an average for the matrix. The measurements were made at a temperature of about 140° above the glass transition temperature of the polymer [43, 44]. The thermal degradation of the polymer is usually studied in the temperature range 300–350 °C [45]. In this temperature range the self-diffusivity of the macromolecules would be greater than the value measured by a factor of between about 6 and 16, assuming that the viscosity-temperature relationship may be extrapolated so far.

The viscosity of polymethylmethacrylate ($M = 6 \times 10^4$) at 150 °C. (About 45–50° above the glass transition temperature of the polymer [44] is 10^7 poise [35]. The self-diffusivity of the macromolecules is then in the neighbourhood of 10^{-14} cm^2 s^{-1}. At about 240 °C we calculate that the diffusivity should be 0.7×10^{-10} cm^2 s^{-1}, very similar to the value obtained for polystyrene. This comparison assumes that the polymethylmethacrylate sample had a narrow range of molecular weight. The correction for the differing molecular weights $(80,000/63,000)^{3.5}$ is about 2.3. The diffusivities in the range used for studies of thermal degradation (250–350°) [46] will be in the range 6×10^{-10} cm^2 s^{-1} to 10^{-8} cm^2 s^{-1}.

The diffusivities of polymers of lower molecular weight are as expected, smaller. The diffusivity of polymethylene in a matrix having molecular weight 5,800 is 1×10^{-7} cm^2 s^{-1} at 150 °C [47].

8. Diffusivities of Small Molecules in Molten Polymers

As with macromolecules in bulk polymer, glass transition temperatures mark a change in the character of diffusion of small molecules in polymer [48]. Values of diffusivities should not, therefore, be extrapolated from measurements made below the transition temperature. The diffusivities of small molecules in crystalline polymers appear to be smaller than those in amorphous polymers, and to depend on the degree of crystallinity in a manner that is not well-established [49]. It seems unwise, therefore, to attempt to extrapolate diffusivities for melts from measurements made on crystalline polymers.

The diffusivities of nitrogen and methane in polyethylene (of unspecified molecular weight) are

similar, and lie between 2.5×10^{-5} to 5.5×10^{-5} cm^2 s^{-1} in the temperature range 125 to 255 °C. [50, 51], showing little variation with temperature. In contrast the diffusivities of methane in polystyrene in the same temperature range lie between 5×10^{-7} and 5×10^{-6} cm^2 s^{-1} [50], and vary markedly with temperature. The diffusivities of n-pentane in polystyrene ($M = 412,000$) in the temperature range 140–170 °C. lie between 2.6×10^{-8} and 1.7×10^{-7} cm^2 s^{-1}. Even over this small range of temperature the diffusivities cannot be represented by an equation of the Arrhenius form. Similar behaviour has been reported for the diffusion of other small organic molecules in polystyrene [52] at these temperatures. The differences in behaviour shown by the diffusivities of methane in polystyrene and polyethylene are easily rationalised. The observations for polystyrene were made little above the glass transition temperature of the polymer (100 °C) [44], whilst those for polyethylene were made well above the glass transition temperature of the polymer (−21 to −125 °C) [53, 30]. It would seem plausible, and has been suggested that [54] an equation of the form applied to the viscosity of macromolecules in polymer melts, might account for the temperature-dependence of diffusivities of small organic molecules in amorphous polymers at higher temperatures. Not all experimental evidence would support the view that there is a simple universal relationship involving T_g for the diffusivities of small molecules in polymers [55]. For members of an homologous series, D should vary approximately inversely with M [32, 56, 57].

Measurements of the diffusivities of small molecules into polymers are most commonly made at, or a little above, room temperature, so that extrapolations need to be made over long ranges of temperature in order to obtain estimates in the region where thermal decomposition is of importance. In summary we believe that at high temperatures (>250 °C) diffusivities of molecules of about the size of monomers have diffusivities of 10^{-6} to 5×10^{-5} cm^2 s^{-1}, and possess small temperature coefficients (probably of the Arrhenius form, with energies of activation of about 4 kcal/mole).

9. Effects of Cross-linking and Swelling of Polymers

Cross-linking of polymers, even to a low degree will effect markedly their diffusion. It also effects significantly the diffusivities of small molecules in them [58]. Conversely the swelling of polymers, or more strictly in the present context, the solution in them of substances of low molecular weight, greatly enhances the diffusivities of both small and large molecules.

10. Rate Coefficients for Diffusion-controlled Reactions

Theoretical expressions for rate coefficients for bimolecular diffusion-controlled reactions are based upon two types of physical model. The first, devised by Smoluchowski [59] and developed by others, [60, 66, 67], evaluates the flux of other reactants towards a chosen reactant molecule. The second, introduced by Rabinowitch, [61] considers the unitary diffusive displacements of the reactant molecules that lead to encounter and reaction. Rabinowitch assumed a quasi-lattice model for the liquid, limiting his treatment of systems of small molecules. Some limitations of this assumption have been avoided in a later "random walk" treatment [62]. Models of the second class suffer the disadvantage of requiring the average length of the unitary diffusive displacement, which is commonly identified with intermolecular separations of small molecules in the liquid state [63].

The Smoluchowski equation is:

$$k_{A,B}(\text{l mole}^{-1}\text{ s}^{-1}) = 4 \times 10^{-3} \pi N_{\text{Av}} D_{A,B} R$$

where R (cm) is the collision diameter for the colliding particles, N_{Av} is Avogadros number, and $D_{A,B}$ (cm^2 s^{-1}) is the mutual diffusivity of A with respect to B. $D_{A,B}$ is the sum of the diffusivities of A and B measured with respect to a common origin.

The Rabinowitch equation may be written:

$$k_{A,B}(\text{l mole}^{-1}\text{ s}^{-1}) = 2z\gamma^{-1} D_{A,B} N_{\text{Av}}/N_0\, \text{l}^2$$

where z in the coordination number for the lattice system (12 for hexagonally close-packed systems), γ, (11/6 for hexagonally close-packed systems [61]), takes account of the fact that not all difusive jumps lead to the separation of the particles from the state of encounter, N_0 is the number of lattice sites in one litre, and l^2 is the mean square unitary displacement of A with respect to B. Multiplying through by l, and assuming that $\bar{\text{l}}\,\text{l}^2 = \bar{\text{l}}^3 = 2^{1/2}(\bar{V}/N)$ [63], we have

$$k_{A,B}(\text{l mole}^{-1}\text{ s}^{-1}) = 2 \times 2^{-1/2} \times 10^{-3} z\gamma^{-1} N_{\text{Av}}\, \text{l}$$

If the lattice model is acceptable the approximations made in deriving this expression are not serious.

The equation for the random walk model is

$$k_{A,B}(\text{l mole}^{-1}\text{ s}^{-1}) = 10^{-3} \nu_j N_{\text{Av}} A\, \text{l}$$

where A is the collision cross section for the reaction, and ν_j is the mean jumping frequency. Elementary laws of diffusion require that $\nu_j = 6 D_{A,B}/\text{l}^2$ [65]. This expression for $k_{A,B}$, and that for ν_j, involve the mean relative jump length and mean square relative jump length, for the diffusion of A relative to B, respectively. In accordance with a simple model, appropriate for small molecules, or for a system that can be regarded as composed of large molecules made up of small segments, we may write $A = \text{l}^2/4$. Assuming that $\bar{\text{l}}^2 = (\bar{\text{l}})^2$ [63] we have

$$k_{A,B}(\text{l mole}^{-1}\text{ s}^{-1}) = (6/4)\pi \times 10^{-3} D_{A,B} N_{\text{Av}}\, \bar{\text{l}}$$

Inserting numerical values into these equations we have (in l mole^{-1} s^{-1} in each case):

Smoluchowski $k_{A,B} = 7.6 \times 10^{21} R D_{A,B}$

$$= 7.6 \times 10^{21}\, \text{l}\, D_{A,B}$$

Rabinowitch $k_{A,B} = 5.5 \times 10^{21} \, \mathfrak{l} \, D_{A,B}$

Random Walk $k_{A,B} = 3 \times 10^{21} \, \mathfrak{l} \, D_{A,B}$

In order to stress the similarity between the equations we have assumed that $R = \mathfrak{l}$, that is the average distance between the centres of mass of the molecules. This is an instructive comparison of the numerical estimates given by the three models, although the simplifying assumptions that have been made are specific to small molecules or to particular models to be discussed later. Even when applied to small molecules, however, some of the assumptions are arguable in relation to real systems. Particular difficulties are involved with the choice of $\tilde{\mathfrak{l}}$, which we have based on a particular lattice model, the relation of $\tilde{\mathfrak{l}}$ as we have defined it, to R, and the relationship of $\tilde{\mathfrak{l}}$ with average diffusive displacements to be related to the diffusivity and distances of separation of reactants during encounter. Only crude estimates of $k_{A,B}$ may be obtained in *a priori* calculations. This is stressed by our rounding off numberical factors in the above equations.

These expressions hold only for extreme diffusion-controlled reactions, and in so far as they are based upon correct assumptions, give maximum values for rate coefficients in liquids.

11. Diffusion-controlled Bimolecular Reactions and their Converse

Consider the sequence of processes: $A + B \; A .. B \; AB$, where $A .. B$ represents the pair of reactants A and B in a state of encounter, or cage, which may be formed at a rate $k_D[A][B]$ from A and B, or at a rate $k_d[AB]$ from AB. The state of encounter may be destroyed at a rate $k_{-D}[A .. B]$ to form A and B, or a rate $k_c[A .. B]$ to form AB. k_D and k_{-D} are determined by diffusive factors. k_D is identical with $k_{A,B}$ in the preceding section. Application of the steady-state condition for $A .. B$, we obtain the rate coefficient for the dissociation of AB to

$$k_{\text{diss}} = k_{-D}k_d / (k_c + k_{-D}); \qquad k_{\text{ass}} = k_D k_c / (k_c + k_{-D})$$

The equilibrium constant for the reaction is given by

$$K_c = [AB]/[A][B] = k_{\text{ass}}/k_{\text{diss}} = (k_c/k_d)(k_D/k_{-D})$$

K_c is determined by thermodynamic factors only, and so are the quantities (k_c/k_d) and (k_D/k_{-D}). Rate coefficients are diffusion-controlled in cases where k_c is comparable with, or greater than k_{-D}. In these circumstances both k_{diss} and k_{ass} are affected by diffusion.

The following question arises, having special significance in macromolecular systems. For diffusion-controlled reactions both k_{diss} and k_{ass} have a dominant dependence upon the mutual diffusivities of the reactants. The terms k_D and k_{-D} in which these dependences appear will be greater for a molecule of given size, if it is formed from (or decomposes into) a large and a small portion, than if it is from (or decomposes into) two parts of comparable size. This arises because, although the form of dependence may be in dispute, diffusivities

of large molecules (and radicals), are inversely dependent upon some power of the molecular weight. The suggestion holds when uniform free diffusion of the particles is allowed. The effect may be enhanced if the macromolecules and their decomposition products are entangled. Such entanglements, of course, directly influence the diffusivities of macromolecules. Provided then that k_c and k_d are less sensitive to the sizes of the reactants than are k_D and k_{-D}, k_{diss} may be greater for reactions that produce a large radical and a small radical, than for those that produce from the same macromolecule, two radicals of comparable size. Does this account for the frequent claims that free radical degradations are initiated by decomposition of end-groups? It appears that random initiation (by breaking of bonds throughout the lengths of the chains) becomes more important at higher temperatures [68, 69]. This could be accounted for on other bases, but is not inconsistent with the hypothesis implied in the present question. Very small radicals would have much smaller energies of activation for diffusion than do larger radicals. Beyond a certain (relatively small) size, however, all radicals would have similar energies of activation for diffusion, although their diffusivities would differ. We will discuss below the nature of the diffusional processes that being into contact the reactive portions of macroradicals, but supposing for the moment that these are determined dominantly by translational diffusion, it is interesting to recall that (translational) diffusivities of small molecules in polymeric systems vary less rapidly with molecular size (as M^{-1}) than do those for larger radicals (which vary as $M^{-3.5}$).

It would, of course, be rash to suppose that k_c and k_d are completely independent of those factors that effect k_D and k_{-D}. k_d can be expected to be determined by the amplitude and frequency of vibrations of a molecule, or a portion of a molecule, about its average position. Such vibrations may affect the intimacy of the interactions between neighbours, and so affect the rate of reaction between such neighbours. The frequency of such vibrations may be determined to some degree by the size of the molecule, and the character of the matrix in which it is situated. Such effects must be small compared with those upon diffusion, but may not be negligible.

12. Estimates of Rate Coefficients for Diffusion-controlled Reactions in Polymer Melts

The expressions for diffusion-controlled rate coefficients may readily be applied to reactions between small molecules. Even if for such reactions there is a requirement that the reactants must assume a certain relative orientation in order that reaction may proceed, it is likely that the necessary condition can be fulfilled during the state of encounter as a result of the rotations which the reactant molecules are able to undergo. If, however, two macromolecules come into contact at a point remote from their reactive centres, it is unlikely that re-

action will take place during the state of encounter. We must consider, therefore, the relative motions of the reactive centres, which are small in comparison with the sizes of the macroradicals. The diffusivities that we have discussed, and which are most commonly studied, describe the displacements of the centres of mass of the molecules. The overall displacement of any part of a molecule during any lapse of time must be the sum of the displacement of the centre of mass of the molecule, and of the displacements relative to the centre of mass (strictly, treated in a vectorial sense). In rigid molecules, displacements of the latter type are due simply to rotations about the centre of mass. In flexible molecules, such as we are concerned with, the effective rotational displacements will commonly be accompanied by significant changes in molecular conformation. We are, therefore, confronted with the problem of the character of the motions of macromolecules that are flexible. The internal motions of flexible macromolecules which lead to changes in conformation, and those which lead to displacements of the whole molecule, are closely interrelated. This question arises in the analysis of the diffusion-controlled reactions of macroradicals in free radical polymerisations. It has been concluded [72] that in such systems the assumption that the mutual diffusivities of the macroradicals' reactive segments may be identified with the mutual diffusivities of the centres of mass of the macroradicals, fails to account for the observed behaviour. It is customary and is generally satisfactory, to regard macromolecules in dilute solution as (equivalent) rigid hydrodynamic spheres [71, 70], in order to account for transport properties, including diffusion. In the present context we require a more intimate understanding of the molecular motions, and it is more satisfying to consider the segment-by-segment displacements [62]. The situation regarding macroradicals in dilute solution in simple liquids remains uncertain, if not "something of a mystery" [67].

Ironically the situation may not be so complicated in systems composed entirely, or almost entirely, of macromolecules. The approved theory for the diffusion of large molecules in such systems [27] seems to be consistent with a sinuous step-by-step movement of the molecules, so that it might be reasonable to use translational diffusivities of the whole molecule to represent the diffusion of constituent segments. If this assumption is incorrect, the estimates of rate coefficients made on its basis, will, insofar as the expressions are otherwise correct, be too small. It is our opinion that any error will not be great.

We have recognised that the reactive centres in macroradicals are small. In estimating diffusion-controlled rate coefficients these "targets" can be regarded as having the dimensions of small molecules, and diameters of about $(3-5) \times 10^{-8}$ cm. In applying the expressions, and regarding the "targets" as spheres we overlook that the reactive centres are not accessible from all directions. Thus our choice of $\bar{e}$ might in any model exaggerate $k_{A,B}$. Using estimates

we have given earlier for diffusivities we find that diffusion-controlled radical-radical rate coefficients for large radicals in melts of decomposing polystyrene are about $10^{5\pm1}$ l mole^{-1} s^{-1}. The (effectively averaged) experimental values for rate coefficients for radical-radical reactions in the corresponding polymerising systems (25–90 °C) are greater, being about 10^6 to 10^7 l mole^{-1} s^{-1} [73]. The rate coefficients for small radicals may be about 10^8 to 10^9 l mole^{-1} s^{-1}, comparable with those in simple organic liquids.

13. Free Radical Concentration in Thermally Degrading Polymers

If a substance C decomposes to form radicals R_1, which are only able to recombine to form C, the $[R_1]_e = ([C]/K_c)^{1/2}$ (following our conventions [12]). $[R_1]_e$ is an equilibrium concentration. We assume that such an equilibrium, and the steady-state concentrations of radicals in the system of interest are attained very rapidly. The utility of this equation will be enhanced if the thermodynamic principles presented earlier in this paper could be consolidated and exploited. In cases of interest the free radicals first formed react and are transformed into other species. Consider first a simple chain reaction, in which a succession of radicals (designated $1, 2, \ldots \ldots$) are formed. The type of reaction is illustrated by polymerisation (without transfer) in which the successively formed radicals are of increasing size, or by degradation reactions (without transfer) in which the successive radicals are smaller. The steady-state concentrations of radicals are given by [74].

$$\sum_i \sum_j k_{t,ij}[R_i][R_j] = k_{in}[C]$$

Let the total concentration of radicals be $[R]_T$, and $[R_i] = y_i[R]_T$ $(\sum_i y_i = 1)$, then

$$[R]_T^2 \sum_i \sum_j k_{t,ij} y_i y_j = k_{in}[C]$$

where k_{in} is the rate coefficient for the dissociation of C into freely dispersed radicals. We may define an average value [75] such that

$$2(k_t)_{av}[R]_T^2 = k_{in}[C]$$

$k_{t,ij}$ and $k_{t,ii}$ and $k_{t,jj}$ for diffusion controlled reactions are related [76, 77, 78]:

$$2k_{t,ij} = k_{t,ii} + k_{t,jj}$$

at least to an adequate approximation, following from the dependence of all expressions for $k_{A,B}$ upon $D_{A,B}(=D_A + D_B)$. The rate of reaction is commonly directly proportional to $[R]_T$. Comparing this quantity with the estimate of $[R_1]_e$ we have

$$[R]_T/[R_1]_e = k_{t,ii}/(k_t)_{av}$$

Thus $[R]_T$ will be larger or smaller than $[R_1]_e$ according as to whether $k_{t,ii}$ decreases or increases with i. In polymerising systems $k_{t,ii}$ falls with the decreasing mobility accompanying the increasing size of the radicals [70]. $[R]_T$ therefore exceeds

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[R$_1$]$_e$. The converse is true in systems in which macroradicals are degrading by the loss of monomer or larger fragments. The effect will probably be more marked in degrading systems than polymerising systems in dilute solution. Values of k_t are proportional to diffusivities. In polymerising systems these would vary approximately as $M^{-1/2}$ [62] if translational diffusion of centres of mass were dominant, but may depend less markedly on M [72]. In polymer melts diffusivities vary as about $M^{-3.5}$ (for larger macroradicals). Unless, contrary to our opinion, complications in the motions of the macroradicals reduce the dominant dependence of diffusion-controlled rate coefficients upon the translational diffusivities of the reactants, we must anticipate some consequences in degradation kinetics on this account. Complications must also follow from changes in D as reaction proceeds.

These generalisations relate to systems in which there are no transfer reactions. When transfer reactions intervene it is more difficult to make generalisations, for it is necessary to know whether the radicals formed by transfer have greater or lesser mobilities than the radicals from which they are formed. In degrading polymers transfer reactions will commonly involve macromolecules, and will produce macroradicals comparable in size with, or larger than, those from which they are produced. This will narrow the range of molecular sizes of the macroradicals, and so minimise the range of values of $(k_{t,ii})$ which determine $(k_t)_{av}$. There could remain, however, a dependence of $(k_t)_{av}$ on the molecular weights of the macromolecule from which the free radicals are derived [79].

14. Geminate Recombination

Our treatment of diffusion-controlled reactions has assumed a random distribution of reactants throughout the volume of the system. Free radicals produced by thermal or photo-decompositions are inevitably produced in pairs. This has the effect already referred to as the converse of diffusion-controlled reaction [61]. If, however, a free radical diffuses away from the primary cage in which it was formed, it will for the earlier part of its "life" lie closer to its geminate partner than to any other free radical. During this time there is significant probability that the twin radicals will encounter and react with one another. Both effects have been called "geminate" recombination [80]. It must be recognised that geminate recombination includes not only the reaction of radicals that have not initiated reaction chains, but also the reaction, with destruction, of chain carriers that have been formed by the successful reaction of free radicals that were created together [81, 82]. Mutual destruction of geminate free radicals that have propagated reaction has an effect upon the kinetics of the overall reaction [81, 83]. The reaction between (nongeminate) free radicals in general is second order with respect to their concentration. The mutual destruction of a geminate pair of free radicals is of first order with respect to their concen-

tration [81, 83]. The second-order process (if exclusive) leads to a dependence of radical concentration upon the square root of the rate of initiation. Geminate recombination (if exclusive) leads to a first power dependence of the concentration of chain-carriers upon rate of initiation [81, 83]. It is likely that the two processes compete [83].

It has been suggested that geminate termination of chains occurs in the thermal degradation of some polymers [84, 85]. In particular it has been invoked to account for an apparent first order termination step observed when degradation of polymer was initiated by a portion of polymer containing deliberately introduced weak bonds [84]. It is desirable that we should examine some characteristics of geminate reactions.

The probability that a free radical will reencounter its twin falls rapidly as the two become more widely separated. Most diffusive jumps lead to increasing separation of the particles. Imagine one of a pair of geminate particles. Only displacements which lie in a direction contained within a small solid angle subtended by the twin particle will lead towards possible reencounter. A crude argument developed on this basis [82] suggests that only about 1/16th of the radicals that escape the primary cage are involved in geminate combination. An important assumption underlying this and other treatments, is that the medium is uniform. Mathematical difficulties arise because we are concerned with random displacements that are not very large compared with the distances to be traversed whilst the geminate partners are close together. Of some importance also might be the effect of the local structure of the medium. Noyes [80, 66] has considered the problem in some detail, and recognised these difficulties. He does not estimate the fraction of radicals that react geminately after leaving the primary cage, but implies that this is small. There has, with some justification, been a call for a better theoretical model [87].

Space does not allow an extensive examination of the subject. We hold the opinion, however, that in uniform systems geminate recombination has only a small effect on the kinetics of propagation. Those radicals that recombine geminately will seldom have propagated the reaction to a great extent. The opinion is based on the frequent observation that rates of reaction are predominantly proportional to the square root of the rate of initiation. Geminate recombination is predominantly a problem in geometry, being the consequence of the distribution of the reactants in the system, and is independent of diffusivity. It may be influenced by local structure, and the occlusion of radicals that has been proposed to account for phenomena in very viscous systems, (more likely to occur in glassy systems than in melts), may result from non-uniformity of structure, about which little is understood [88].

Further support for our view comes from the generation of free radicals from mixtures of initiators [89]. If two initiators, one generating radicals of type R$_1$ and the other radicals of type R$_2$, then products of the type R$_1$R$_2$ can only be formed by

radicals that have escaped geminate reactions (either in the primary cage, or secondary reactions). If it is supposed that the chances of encounter and reactions between pairs of freely diffusing radicals is statistical, as in the gas phase, and as it is likely to be in solution is the radicals R_1 and R_2 are sufficiently similar to have almost equal diffusivities, then we would expect that the distribution of products would be such that, for the products of reaction

$$[R_1R_2]/[R_1R_1]^{1/2}[R_2R_2]^{1/2} = 2$$

Studies in solution have shown that the products do not conform to this statistical requirement. If [89] the deviations from statistical requirement are attributed to geminate reactions. In different types of measurement, Szwarc and his co-workers [87] have shown that up to 70 percent of the radicals formed from azo-ethanes undergo geminate recombinations. These proportions are unusually high, compared with initiators used in polymerisation [90, 91]. These measurements include the proportion of radicals that react in the primary cage, and which, because they react mutually so quickly, are unable to propagate the reaction. They do not, therefore, invalidate the opinion just given.

The results of a careful investigation of the polymerisation of vinyl acetate [92] show that at low conversions about 10 percent of propagating radicals terminate by a first order process, that is probably geminate [83]. At higher conversions (above about 40 percent) in the same reaction, when the system is very viscous, a different type of first order destruction of radicals takes place, probably due to microheterogeneity of the gel [83]. The contribution made to the overall reaction by free radicals that react geminately clearly depends upon their reactivity. Radicals may react geminately with or without having propagated reaction. In degrading systems the most significant reaction of the radicals is to eliminate a portion of themselves. This has the effect of increasing the distance, and number of molecules, between the geminate partners. The small products of the reaction may, of course, diffuse away rapidly. The effect may reduce, but certainly not enhance, the contribution of geminate reactions to the overall kinetics.

It is of interest to examine whether the diffusive displacements undergone by a degrading macro-radical compare with the displacements of the reactive centre resulting from the extrusion of a fragment from the radical. The rate coefficient for the expulsion of a monomeric (or larger) unit from a macroradical is unlikely to exceed about $10^{14} \exp[-25,000/RT]$ s^{-1} (R in cal deg^{-1} mole^{-1}) [96]. At about 400 °C the mean lifetime of the radical with respect to this process is about 10^{-6} s. Assuming a low value of diffusivity, about 10^{-10} cm^2 s^{-1}, the rms displacement due to diffusion is about 10^{-8} cm. This is small compared with the contraction in size of the radical, and may be interpreted as indicating that only a fraction of the radicals (or, more strictly, of their centres of mass) have moved significantly during the time required for reaction. The figures

chosen for this calculation are extreme. It might be that conditions can sometimes be realised in which there is competition between diffusion and decomposition in displacing reactive centres. The situation seems to differ from most polymerisation systems.

15. Loss of Radicals by Evaporation

Studies of the degradation of polymers are frequently made using thin films, often of thickness of 10^{-2} to 10^{-3} cm. It is proper to ask whether in such circumstances the more mobile free radicals may evaporate from the system, so contributing effectively a first order process for the destruction of radicals. The suggestion has frequently been made. Recently [86] a detailed mathematical analysis has been made of the problem. A simple approach is now made to the assessment of the likely importance of the process. The radicals will most readily be lost by this process if they evaporate so efficiently from the surface that their concentration at the surface is zero. Consider a slab of thickness b, from which evaporation may take place at one surface ($x=b$) and within which the radicals are produced at a uniform rate I (radicals per unit volume) [93, 94]. The average steady-state radical concentration is $Ib^2/3D$. The average lifetime of radicals for this process (average concentration/rate of production) is $b^2/3D$. The highest diffusivities likely to be encountered are about 10^{-5} cm^2 s^{-1}. If $b=5\times10^{-3}$ cm, the lifetime is about 10^{-1} to 1 s. The lifetime with respect to homogeneous second order destruction of radicals is about $(k_t[R])^{-1}$. (Here [R] is the total concentration of radicals). Values of k_t, even for reactions involving small radicals, are unlikely to exceed 10^9 l mole^{-1} s^{-1}. We take $[R]=10^{-8}$ mole l^{-1} [95]. The lifetime for destruction of the small radicals by this process must be larger than 10^{-1} s. The two processes could be important where degradation produces small radicals.

16. Final Comments

The study of reactions of small molecules, in the gas phase, provides information about the simple reaction steps, such as transfer reactions, and elimination of olefins, that are involved in free radical degradation of polymers in melts. In few cases, however, do the studies of the thermal decomposition in the gas phase provide information that may be compared directly with the kinetics of degradation of polymers in melts. There is one case in which a direct comparison might be profitable. This is the pyrolysis of larger hydrocarbons, which have been studied for its industrial importance, and which might usefully be compared with the thermal decomposition of polymethylenes. There is evidence that the decomposition of hydrocarbons in the range C_{10} to C_{30} is not a first order process, and the overall kinetics may be interpreted [97] on the basis of proportionality to [hydrocarbon]$^{1.3}$. This indicates the complexity of the reaction, but is an empirical simplification. Clearly the pyrolysis involves many

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reaction steps, which include transfer, and a diversity of termination reactions. This is also true of the decomposition of polymethylenes. Isomerisations of free radicals which are important in both decompositions, and which have been discussed recently [98, 99] may differ, on account of reduced mobility in the melts.

17. Notes and References

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[12] Consider a system comprising n_i moles of each of a set of components $(i = 1, 2, \ldots)$ having partial molar volumes V_i. The total volume is given by $V_T = \sum_i V_i$, where the summation, here and later, is made over all components. The total number of moles in the system is $n_T = \sum_i n_i$. We may define an average molar volume for the system $V_s = V_T/n_T$. The mole fractions are defined by $x_i = n_i/n_T$. The concentrations may be written $c_i = n_i/V_T = n_i/n_T V_s = x_i/V_s$. Comparison of the expressions for K_c and K_x give the result quoted in the text. We have consistently written K_c $(=c_{AB}/c_A c_B) = [AB]/[A][B]$; $K_x = x_{AB}/x_A x_B$. We are aware of the practice in degradation studies of expressing concentrations in alternative forms, e.g. in terms of mole per base mole. We have not considered it worthwhile to develop our arguments in these alternative terms.
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$$\alpha = V_s^{-1}(\partial V_s/\partial T)$$

is the coefficient of expansion of the solution. The corresponding entropy change is

$$\Delta S_c = \Delta S_x + \Delta n R \ln V_s + \Delta n \alpha RT.$$

The terms containing α are often small, and may be neglected in comparison with experimental error. The equation for ΔH_c was given by Guggenheim, E. A., Trans. Farad. Soc., 33, 607 (1937).

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[75] Consistent with our assumption, write $k_{t,ij} = g_j$; then

$$(k_t)_{av} = \sum_i \sum_j (g_i - g_j) y_i y_j = 2 \sum_i \sum_j g_i y_i y_j = 2 \sum_i g_i y_i$$

If $g_{i+1} > g_i$, all i, then $(k_t)_{av} > k_{t,ii}$; and conversely.

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$$J(b) = +D(d[R]/dx)_b = +Ib.$$

Total loss of radicals by evaporation must equal rate of generation. The solution is $[R] = I(b^2 + x^2)/2D$.

[94] It is tempting to ask whether in such films the surface on which the film is deposited may influence the reaction.

[95] This is a guess, in our experience $[R]$ seldom is much greater than 10^{-8} mole l^{-1}.

[96] Preexponential factors for most free radical decomposition (of the type we are considering lie in the range 10^{12} to 10^{14}s^{-1}, and are often closer to the lower limit. They are usually associated with larger energies of activation (closer to 30 kcal mole^{-1}). For recent values see Kerr, J. A., Ann. Rep. C.S., **65**, 189, 64, 73.

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Discussion

R. E. Florin (National Bureau of Standards):

It would appear that many discussions of diffusion-controlled reactions of polymers focus on the motion of chain ends. Segments in the middle of a polymer chain ought to have lower diffusion-controlled reaction rates than those at chain ends. Computer simulations of polymer segment diffusion [P. H. Verdier, J. Chem. Phys. **52**, 5512 (1970); J. Computational Phys. **4**, 204 (1969)] could in time lead to some estimate of the difference. I would be interested in Dr. Patrick's view of this question.

Dr. C. R. Patrick, University of Birmingham, England (communicated).

In my paper I have discussed briefly the diffusive motions of macromolecules. Whilst admitting the possibility that the overall diffusive displacements of the segment of a macromolecule in a given time may be greater than those of the centre of mass of the whole molecule, I ventured the opinion that the diffusion of a segment of a macromolecule may be described by the diffusivity of the centre of mass of the molecule without too great and error. This practice was followed in subsequent calculations. Some further comments on this question may be appropriate.

Macromolecules or macroradicals of interest are flexible and able to take up a large number of alternative configurations. In detailed treatments of dynamic properties of macromolecules, particularly those relating specifically to diffusion and changes in configuration, a macromolecule is regarded as composed of a set of segments, linked together, but each of which may move independently of other segments. Some models regard the molecule as composed of segments, all equal in size, arranged so that the centre of mass of each segment is located on a lattice point. Diffusion occurs by the jumping of a segment to an adjacent site on the lattice. It may be shown [1] that such a model requires that the diffusivity of the centre of mass of the macromolecule, $D_{c.o.m.}$, is related to that of any segment, $D_{segment}$, by

$$ND_{c.o.m.} = D_{segment} \qquad \text{eq 1}$$

where N is the number of segments in the macromolecule. The detailed proof of this equation, as usually given, follows from the expression of the diffusivity ascribed to each segment in terms of the friction coefficient involved [1, 2]. Whilst this is clearly correct, the equation may be derived more directly. Consider a macromolecule composed of N segments, each of which has a diffusivity $D_{segment}$. It may readily be shown that any displacement, δ, undergone by a segment, must cause a displacement (δ/N) of the centre of mass of the molecule [2]. Assuming that all unitary length, we may write

$$D_{segment} = \nu \delta^2 / 6$$

where ν is the jumping frequency, so that for the centre of mass

$$D_{c.o.m.} = \nu N (\delta/N)^2 / 6$$

from which eq 1 follows immediately.

It is normally assumed that the segments are equally free to move, and are of equal size. These assumptions may not always be realistic. It is possible, for example, that the motions of some segments may be impeded by other portions of the same molecule. If this possibility is recognised, eq 1 may be generalised to give

$$ND_{c.o.m.} = (D_{segment})_{av}$$

where the latter term is an average of all segmental diffusivities. In such circumstances it would be difficult to know the diffusivity of a particular segment which contains a centre of chemical reactivity.

The definition of a segment as a portion of a macromolecule that is able to move independently, is a convenient mathematical device. A segment cannot readily be identified with a specific chemical unit within the molecule. It cannot, for example, be identified with a monomer unit in a polyvinyl compound. The property of independent movement ascribed to segment imposes a severe stricture upon the motions of segments within the polymer chain. Such motions are limited to changes of conformation of a segment without moving the positions of its ends, and to rotational motions of a segment about the line joining its ends. It is conceivable that a particular atom in a macromolecule may move (in a diffusional manner) with different combinations of other atoms in successive jumps or sequences of jumps. The definition of a segment, when generalised, has a statistical character, similar to that of the subunit of a macromolecule considered in the enumerations of the statistics of chain configurations. It would be unwise, however, generally to identify a segment in the present context with the unit involved in chain configurations. Evidence for the sizes of segments, and the relation of N to molecular weight, must be sought elsewhere, and may, perhaps be found in the analysis of other dynamic properties of polymers.

Equation 1 has the satifying property that it allows for the mobility of segments within a very large molecule, such as may occur in a cross-linked system. The movement of the centre of mass of such a molecule may be barely perceptible although displacements of its constituent parts may be significant (as may be seen by setting N equal to infinity). Clearly the setting of N equal to unity is equivalent to regarding the molecule as rigid. Alternatively, as an excellent approximation we may write $D_{c.o.m.} = D_{segment}$ for the special case, referred to in the paper, in which the diffusion of a macromolecule proceeds by segment-by-segment displacements, in which the end segment of the molecule may move forward and drag all other segments behind it, so that each moves to the space previously occupied by its nearest neighbour. Since the end of

the molecule first to move in a displacement may move into any of a (possibly small) number of positions, each displacement must lead to a new conformation of the molecule, so that over the course of time the molecule may take up all the accessible conformations.

The consequences of eq 1 in radical-radical reaction kinetics need to be considered (for the possible cases that $N \neq 1$). Assessment is needed of the error involved in making the assumption, previously made, that $D_{c.o.m.} = D_{segment}$. It is needed both for reactions between macroradicals in melts and in solution in simple liquids. The problems in the two cases may differ. For example the diffusivities of macromolecules in simple liquids vary approximately as (molecular weight)$^{-1/2}$ (see references in paper). Since (unless $N=1$) we would expect N to be proportional to molecular weight, it follows that $D_{segment}$ should approximately be proportional to (molecular weight)$^{1/2}$, which appears absurd, and poses a problem for closer examination. The difficulty

is related to the fact that eq 1 is essentially related to the so-called "free-draining" model for macro-molecules in solution [3], whilst the simple transport properties of macromolecules in solution are better accounted for in terms of "equivalent hydronamic spheres" [4, 5]. The situation is further complicated by the finding that viscoelastic properties of polymers in dilute solution are satisfactorily accounted for in terms of the free-draining model [6].

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Pyrolysis of Polymers

Leo A. Wall

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

The nature of their pyrolysis products, monomer, oligomers and carbonaceous residues enables one to group polymers into three classes, those that decompose by net main chain scission; by stripping of the main chain, for example the thermal dehydrochlorination of polyvinyl chloride; and by crosslinking of the main chain followed by some production of volatiles. Highly unsaturated or aromatic chains tend to follow the latter course.

At the present time a theoretical framework exists which permits, provided adequate experiments are performed, the elucidation of the decompositions of the first type. For most of the well-known polymers in this class, this framework of knowledge gives very acceptable mechanistic explanations or interpretations of the decomposition process based on observations of rate of weight loss, of molecular weight changes and composition of volatile products.

Knowledge of the decomposition of the second class of polymers is at an intermediate state development. However, an important practical research objective would be the acquisition of methods for converting the mechanisms of decomposition of class one substances to that for class two type.

For the third class of materials, knowledge of their pyrolysis mechanisms is nonexistent. This is largely due to the fact that methods for quantitatively following solid-phase processes of decomposition are relatively difficult and unsatisfactory.

Key words: Chain scission; crosslinking; polymers; pyrolysis; stripping.

Under vacuum or moving inert atmospheres polymers decompose to produce volatile products and char to various degrees [1, 2, 3].[1] Polymers can be divided into three groups according to the characteristics of their decomposition process (see table 1).

1. Saturated Polymers

The saturated vinyl type polymer decomposes either by some form of chain scission or by the loss of some substituent group through a chain stripping reaction. The type of reaction is determined by which bonds in the molecule are most easily thermolyzed. If the bond to a substituent is easily ruptured, we get a dehydrohalogenation type reaction leaving an unsaturated and possibly aromatic carbon system which then crosslinks to form
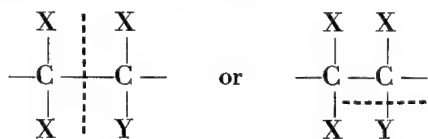
eventually a carbonaceous char. On the other hand, if a carbon-carbon bond ruptures, we get sometimes monomer, but more often a variety of products, including dimer, trimer, etc. Table 2 lists monomer yields for some linear polymers and heats of poly-

merization. It is clear that the more substituted structures give higher monomer yields. They also have low heats of polymerization, degrade under high energy radiation, and are the least thermally stable. This generalization is true only if we restrict ourselves to hydrocarbon polymers. Polytetrafluoroethylene yields, under high vacuum conditions, 100 percent monomer and has a heat of polymerization of 40 kcal. The precise mechanism of decomposition for substantially pure polymer would, of course, depend on temperature among other things.

It would also depend on the pyrolytic procedure and the geometrical arrangement of sample and furnace. In order to emphasize the effect of molecular structure, our studies are usually carried out by following the rates of volatilization or vaporization under high vacuum conditions by recording the weight of sample lost (gravimetry).

Vaporization phenomena can be divided into three categories depending on the particular step in the process that is rate controlling. The three categories are: (1) rate proportional to surface area, (2) rate proportional to surface area and inversely proportional to thickness, and (3) rate proportional to weight of sample. The first category is simple molecular vaporization in which the rate determining step is the escape of well-defined molecules from their liquid or solid phase into the gaseous phase. At a given temperature the rate of volatilization depends on the fraction of molecules in the surface layer that have an energy equal to or greater than

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Types of thermal decomposition*

Type	Products	Examples
Chain scission	$\leq 99\%$ volatile monomer Species <2000 M_n	$\sim CF_2CF_2\sim\rightarrow CF_2CF_2$ $\sim CH_2CH_2\sim\rightarrow$ alkanes + alkenes $\sim CH_2CH\sim\rightarrow CH_2=\overset{H}{\underset{}{C}}$, Di, trimer, etc.
Stripping	Volatiles and char	$\sim CH_2CHCl\sim\rightarrow HCl +$ aromatics + char $\sim CH_2CF_2\sim\rightarrow HF +$ aromatics + char
Crosslinking	Little volatiles, much char	

the minimum kinetic energy needed for escape from the surface. In the case of water, or pentane, the kinetic energy must be greater than the energy resulting from the Van der Waals type of attractive forces. In the case of a metal the process is the same except the attractive forces between the metallic atoms are larger than the usual Van der Waals forces. One may also consider diamond volatilizing as C atoms, except that diamond converts to graphite between 500 to 1000 °C and does not volatilize to give 100 percent pure C atoms but probably gives various amounts of C_2, C_3 species, depending on conditions.

These systems differ basically in the amount of energy involved in the evaporation process. In each the overall process is:

$$A_{\text{liquid or solid}} \overset{k_v}{\rightarrow} A_{\text{gas}}.$$
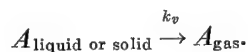
Few, if any, studies of polymer degradation are concerned with establishing whether the process under study is obscured by molecular vaporization or by diffusion processes. The molecular vaporization of large organic molecules has been examined by us in order to determine the upper molecular weight limit for molecular vaporization without decomposition for various organic structures. We believe information in this area is critical for the full elucidation of polymer pyrolysis.

2. Molecular Vaporization

The molecular vaporization of three groups of compounds have recently been investigated. They are (1) various organic plasticizers [4], (2) normal alkanes [5], and (3) various triglycerides and sebacate esters [6].

According to kinetic theory the rate of condensation, dn/dt, of a vapor in moles per sec is given by [7]

$$\frac{dn}{dt} = \frac{\alpha p A}{(2\pi MRT)^{1/2}}, \qquad (1)$$

where α is the accommodation coefficient, assumed here to be one; p the pressure, dynes per cm², of the substance in the gas phase; A the surface area, cm²; M the molecular weight; R the gas constant in ergs per degree Kelvin; and T the absolute temperature. Since, when a vapor and liquid phase are in equilibrium, the rate of vaporization equals the rate of condensation, we can write the same equation for the rate of vaporization except that now p is the equilibrium vapor pressure at the temperature T. The rate of vaporization we are concerned with is that measured under vacuum conditions and is sometimes referred to as the maximum rate of vaporization. Since the vapor pressure, in atmospheres, is the equilibrium constant for the process, we may write

$$P_v = e^{-\Delta F_v/RT} = e^{\Delta S_v/R}e^{-\Delta E_v/RT}e^{-P\Delta V/RT}. \qquad (2)$$

For one mole of vapor, $P\Delta V = RT$, and hence the rate of volatilization, can be written as

$$\frac{dw}{dt} = 16.25\left(\frac{M}{T}\right)^{1/2} Ae^{\Delta S_v/R}e^{-\Delta E_v/RT}, \qquad (3)$$

where dw/dt is the rate of vaporization in grams per second assuming that α, the accomodation coefficient, is one. From the preceding relationship, the Arrhenius slope is found to be

$$\frac{d\ln(dn/dt)}{d(1/T)} = \frac{T}{2} - \frac{\Delta E_v}{R}. \qquad (4)$$

From our rate measurements then we can obtain, according to kinetic theory, the internal energy, ΔE_v, for vaporization and also the enthalpy ΔH_v. If the apparent Arrhenius activation energy is designated as $\mathcal{E}_v$, then

$$\Delta E_v = \mathcal{E}_v + \frac{RT}{2}$$

and

$$\Delta H_v = \mathcal{E}_v + \frac{3RT}{2}$$

since

$$\mathcal{E}_v = \frac{-Rd\ln(dn/dt)}{d(1/T)}. \qquad (5)$$

Using these relations and our observed apparent activation energies, values were calculated for the

48

enthalpies of vaporization ΔH_v at the mean temperature of our experiments. For n-pristane, n-tetracosane, n-hexatricontane and n-tetranonacontane the values were 18, 23, 29, and 47 kcal/mol, respectively, and did not appear to be in line with literature values at first sight.

In order to evaluate our experimental data and hence our technique, we reviewed and recalculated values of ΔH_v from data [8–17] in the published literature. The most extensive source of original data was the compilation made by Stull [8]. Direct calorimetric or Knudsen technique measurements were available for only a limited number of alkanes, C_7 to C_{18}, and only at a single temperature. The bulk of the ΔH_v values obtained were from vapor pressure versus temperature data either in its original form or in the form of the Antoine equation. Examples of the latter are those found in reference [9].

Greatest weight was given to ΔH_v values determined from original vapor pressure data through the slopes of $\log p_v$ versus $1/T$ plots at selected temperature, viz., 0, 50, 100, 150, 200, and 250 °C using the Clapeyron equation corrected for the compressibility factor ΔZ. The relationship is

$$\Delta H_v = -2.303 R \Delta Z \frac{d \log p_v}{d 1/T}. \qquad (6)$$

Estimates of ΔZ as a function of $1/T$ are tabulated [18] in the literature. This tabulation is apparently based on the relationship

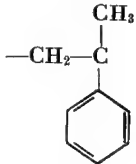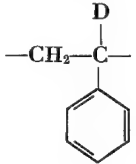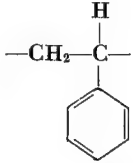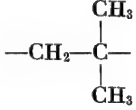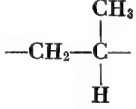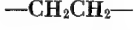$$\frac{PV}{RT} = 1.0 - 0.05 P(\text{atm}) \qquad (7)$$

at 25 °C. As no values of p versus T data above 1 atm pressure were used in deriving ΔH_v values, ΔZ was always >0.95. The error associated with this method should be no greater than 1.5 percent at 1 atm.

The calculated ΔH_v values were first plotted as a linear function of the number of carbon atoms, n, in the alkanes. Over a range of species with 4 to 24 carbon atoms the plots for several different temperatures did not yield straight lines. The data appear to be best fitted by straight lines for every eight or so consecutive species as shown. The breaks in linearity seem to occur at about every 7–8 carbon atoms. This suggested a coiling or folding of the vaporizing molecules as was predicted by Langmuir [19]. Also, Huggins [20] in 1939 predicted that the heats of vaporization of linear alkanes should vary as the 2/3 power of the number of carbon atoms. Therefore, we plotted the data as a function of $n^{2/3}$ and obtained excellent straight lines. It was evident that at a given temperature the variation in heats of vaporization for the linear alkanes is very closely approximated by a linear function of the 2/3 power of the number of carbon atoms. The straight lines obtained are given by the relationship

$$\Delta H_v = 3.21 n^{2/3} - 0.0193 T + 2.92, \text{kcal/mol}, \qquad (8)$$

where T is degrees Kelvin.

TABLE 2. *Monomer yield from the decomposition of polymers*

Polymer	Structure	Monomer yield Wt. %	Heat of polymerization *Kcal*
α methyl styrene	$-CH_2-\underset{\underset{\bigcirc}{\overset{CH_3}{\mid}}}{C}$	99	9
α deuterostyrene	$-CH_2-\underset{\underset{\bigcirc}{\mid}}{\overset{D}{C}}-$	70	17
styrene	$-CH_2-\underset{\underset{\bigcirc}{\mid}}{\overset{H}{C}}-$	42	17
isobutylene	$-CH_2-\underset{\overset{\mid}{CH_3}}{\overset{CH_3}{\overset{\mid}{C}}}-$	25	15
propylene	$-CH_2-\underset{\overset{\mid}{H}}{\overset{CH_3}{\overset{\mid}{C}}}-$	2	17
ethylene	$-CH_2CH_2-$	0.1	22

The $n^{2/3}$ function is highly acceptable on the physical basis that a linear molecule will find it energetically easier to vaporize when coiled into a sphere than as a long extended molecule. The spherical model entails the rupturing of a minimum amount of Van der Waals bonding during the vaporization process. According to this model and the above equation, the increment in ΔH_v per carbon atom or methylene group decreases with the size of the molecule. By differentiating eq (8) with respect to n, it follows that the increment in ΔH_v per carbon atom is found.

$$\Delta(\Delta H_v) = 2.14 n^{-1/3}.$$

Thus, the increment at 10^3 carbon atoms is 214 calories per mole.

In table 3 we summarize our experimental data and show the numerical agreement between the experimental activation energies and values calculated from the equation

$$\mathcal{E}_v = 3.21 n^{2/3} - 0.0223 T + 2.92, \text{kcal/mol}. \qquad (9)$$
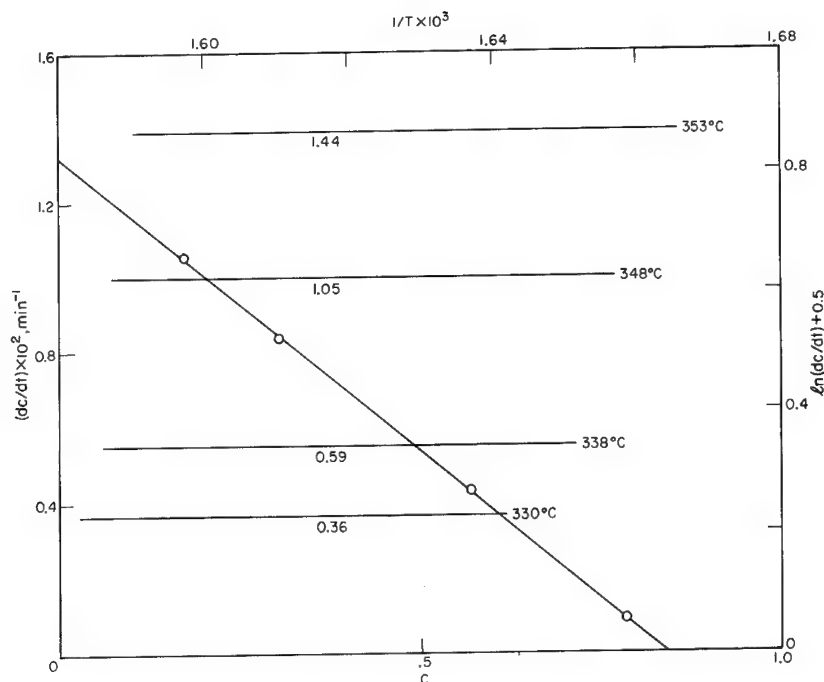
Both the experimental and calculated values are

FIGURE 1. *Rate of vaporization of tetranonacontane* ($C_{94}H_{190}$) *and Arrhenius plot of data, activation energy 46 kcal/mol (quartz bucket 10×4 mm i.d., 10 mg sample)* [5].

compared at the mean experimental temperature, T; see last column. The agreement is very good particularly for the three smaller compounds and supports our premise that correct values of the energies of vaporization can be obtained quickly with the presently available equipment. The low result for the largest species, the C_{94}, is still quite good considering the degree of extrapolation involved. At such a high n value, one suspects that eq (8) will give high values since one anticipates spheres of greater density, the greater the value of n. Experimental rates of vaporization at the temperature given in the last column are also listed.

The rate of decomposition [21] of polyethylene is usually measured in the region of 400 °C and is proportional to the weight of polymer, not to surface area. The products of thermal volatilization of linear polyethylene assuming a random mechanism indicate [41] that 72 carbon atom species are about the minimum size that decompose before evaporating. From eq (8) it follows that the internal energy ΔE_v for vaporization at 400 °C is for $n = 72$, 43.5 kcal; for $n = 129$, 70 kcal; and for $n = 154$, 80 kcal. The value 43.5 kcal is closer to the activation energy values of the possible free radical decomposition reactions constituting part of the overall thermal decomposition mechanism. The actual overall activation energy for thermal decomposition is about 70 kcal and the usual carbon-carbon bond dissociation energy is 80 kcal. These results show that molecular vaporization of linear alkanes comprised of 100 or so carbon atoms can occur without decomposition. For several experiments with the C_{94} compound a gravimetric apparatus with an attached mass spectrometer, capable of monitoring masses from 12 to 120, was used and no hydrocarbons from

the C_{94} sample were observed. This supports, as does the observed kinetic behavior, the conclusion that the C_{94} volatilized molecularly without appreciable thermal decomposition. In figure 1 we show both the rate of vaporization for tetranonacontane ($C_{94}H_{190}$) as a function of fraction vaporized, the horizontal line typical of molecular vaporization, and the Arrhenius plot of the data, the open circles.

Up to molecular weights of $\sim$900 the energies of vaporization of both the branched triglycerides and the linear sebacate esters follow rather closely the curve for the linear alkanes, i.e., eq (8) [6]. This again is presumably a result of the coiling of the molecules, both branched and linear, into spheres of similar size during the vaporization process.

3. Diffusion Controlled Vaporization

Vaporization may in some cases be diffusion controlled, the second category. In the extreme limit, if every vaporizable molecule leaves the exposed surface immediately, then the rate at which they arrived at the surface determines the rate of vaporization, for example, a volatile organic liquid in a plastic vessel. The rate of vaporization would, in the simplest case, be proportional to the outer surface area and inversely proportional to the wall thickness of the vessel. This kind of process is rare in studies of polymer pyrolysis, where sample size and thickness are kept small in order to eliminate the effect. It can produce delayed effects during the start up [22] or stoppage of pyrolytic processes. For example, monomer [22] or other products must build up to a steady state concentration before the steady rate of volatilization is achieved. Here we have essentially digressed to the questions of ordinary diffusion of

small molecules through polymer. Later on we shall mention several ways diffusion can alter the competitive situation between the various elementary reactions in the degradation mechanisms.

4. Degradative Vaporization

The third category, in which we have been most interested in the past, applies in general to practically all high polymers. Because polymeric solids or liquids are, in the main, long linear molecules, the vaporization phenomenon is basically different from say graphite or water. Polymer molecules are, in general, too large for vaporization to occur without decomposition of the molecules. Thus, high polymers degrade to relatively low molecular species in order to volatilize. Chemical bonds must break, which they do by a variety of mechanisms. Regardless of the mechanism, however, the rate of volatilization is determined basically by the rate of bond rupture. Since the number of bonds is proportional to the weight of material, rates of volatilization for polymers are, ideally, proportional to the weight of polymer, not to the surface area or thickness. The rate determining step in the volatilization process for high polymers having no low molecular weight impurity is the degradation process. This is not to say that, depending on various factors and conditions, diffusion phenomena may not play some role in retarding the overall evaporation or altering the mechanism and products of polymer degradation.

Schematically, then:

polymer $\xrightarrow{\text{degradation}}$ small molecules (cond. phase) $\xrightarrow{\text{diffusion}}$ small molecules (at surface) $\xrightarrow{\text{evaporation}}$ small molecules (gas).

In a particular system, diffusion or evaporation can be rate controlling. With high polymers, degradation is usually rate controlling but this should be confirmed experimentally.

The critical size, $L-1$, above which degradation should occur, has been roughly estimated in the past by equating the heat of vaporization to the bond strength, $9.92 + 1.18(L-1-8) = 80$, where 80 is the usual carbon-carbon single bond strength in kilocalories, 9.92 is the heat of vaporization of octane, and 1.18 is the increment above n-octane in the heat of vaporization per methylene unit. The value thus obtained for $L-1$ is 67 which is close to the value of 72 deduced from experimental data on the thermal volatilization of polyethylene. Recent work has shown that the heats of vaporization of the n-alkanes are not linearly proportional to the size of the alkanes. Based on the new studies the heat of vaporization of 72 carbon atom alkanes is approximately 44 kcal/mol.

Experimentally, we define the conversion, i.e., the fractional weight lost, in terms of the weight, W, of the polymer

$$C(t) = 1 - \frac{W(t)}{W(0)} . \qquad (10)$$

In theoretical treatments for the volatilization of monodispersed molecules, each containing N units, we write

$$C(t) = 1 - \frac{\sum_{L}^{N} i Q_i(t)}{N Q_N(0)} . \qquad (11)$$

It is readily seen from the term with the summation sign that L is defined as the smallest species which must decompose in order to evaporate. For the same system the number average degree of polymerization is given by

$$\bar{P}_n(t) = \frac{\sum_{L}^{N} i Q_i(t)}{\sum_{L}^{N} Q_i(t)} \qquad (12)$$

Rates of decomposition of the polymers would, in general, be measured at temperatures where the rate of weight lost is approximately one percent per minute. In the vicinity of these rates the mechanisms of decomposition involve a competition between the monomolecular dissociation of intermediate radicals to monomer and smaller radicals and the bimolecular transfer reaction illustrated below [23, 24]. Since in what follows only cases with one type of initiation and one type of bimolecular termination are treated, the rate constants for the particular type of reaction are not given unique symbols.

Depolymerization Mechanisms

Initiation		
End	$Q_i \rightarrow R_{i-1} - R_1$	$2k_1 \sum Q_i$
Random	$Q_i \rightarrow R_{i-j} - R_j$	$2k_1 \sum_i Q_i$
Propagation	$R_i \rightarrow R_{i-1} - M$	$k_2 \sum R_i$
Intermolecular Transfer	$R_i + Q_j \rightarrow Q_i + Q_{j-k} + R_k$	$\frac{k_3}{V} \sum R_i \sum j Q_j$
Termination		
Disproportionation	$R_i + R_j \rightarrow Q_i + Q_j$	$\frac{2k_4}{V} [\sum R_i]^2$
Combination	$R_i + R_j \rightarrow Q_{i+j}$	$\frac{2k_4}{V} [\sum R_i]^2$
Monomolecular	$R_i \rightarrow Q_{i-s} + R_s \uparrow$	$k_{4s} \sum R_i$
Caged Combination	$R_i + R_j \rightarrow Q_{i+j}$	$k_{4c} \sum R_i$
Caged Disproportionation	$R_i + R_j \rightarrow Q_i + Q_j$	$k_{4d} \sum R_i$

Polymer molecules and radicals are, respectively, designated as Q_i, Q_j, R_i, R_j, etc., where the subscripts indicate the number of monomer units in the molecule. Monomer is given the symbol, M.

No closed form relation can be derived for the entire set of equations shown above. To evaluate experiments, one must use a computer to numerically evaluate specified cases [25, 26]. However, many

TABLE 3. *Activation energies for the molecular vaporization of n-alkanes* [5].

Alkane	n	M	Rate, g/cm² s $\times 10^5$	ε_v, kcal/mol		$\overline{T}$ °C
				Expt.	Eq (9)	
n-pristane	19	268	6.0	18	18.9	35
n-tetracosane	24	338	6.8	21	21.9	75
n-hexatricontane	36	506	7.5	29	28.6	145
n-tetra-nonacontane	94	1318	12.0	46	55.6	345

polymer decomposition mechanisms can be evaluated by comparison with theoretical relations derived from simplified mechanisms which are special cases of the more complete system of reactions. At least 25 useful and easily deduced special cases can be treated.

5. Decomposition of Polystyrene

In what follows, we will present only two cases; one which is applied to polystyrene data follows immediately. Later on, a second case is presented and applied to polytetrafluoroethylene data.

Assume new polymer molecules are only produced by transfer.

$$\frac{dQ}{dt} = \frac{k_3 R(t) \bar{P}_n(t) Q(t)}{V(t)} \tag{13}$$

where Q represents all polymer molecules, $\bar{P}_n$ the number average degree of polymerization, and V the volume of polymer. All these quantities depend on time. It can be shown that

$$\frac{dQ}{dt} = \frac{k_3 \rho V(t)}{V(t) m} R(t) = k_3 \frac{\rho}{m} R(t). \tag{14}$$

Here, ρ is the density and m the molecular weight of monomer. The rate of conversion to volatiles, assumed here to be only monomer, is given by

$$\frac{dC}{dt} = \frac{m}{w_0} \frac{dM}{dt} = \frac{m}{w_0} k_2 R(t). \tag{15}$$

Combining eqs (14) and (15) gives

$$\frac{dQ}{dC} = \frac{k_3 \rho w_0}{k_2 m^2}, \tag{16}$$

which integrates to

$$Q(t) - Q(0) = \frac{k_3 \rho w_0}{k_2 m^2} C. \tag{17}$$

Since $Q(t) = w(t)/m\bar{P}_n(t)$, eq (5) becomes

$$\frac{1-C}{\bar{P}_n(t)} - \frac{1}{\bar{P}_n(0)} = \frac{k_3 \rho}{k_2 m} C, \tag{18}$$

or

$$\frac{\bar{P}_n(t)}{\bar{P}_n(0)} = \frac{1-C}{1 + \dfrac{\bar{P}_n(0) k_3 \rho C}{k_2 m}} \tag{19}$$

Assuming a steady state and equating end initiation with termination by disproportionation,

$$\frac{k_1 \rho V(t)}{m P_n(t)} = \frac{k_4 R(t)^2}{V(t)}, \tag{20}$$

we find

$$R(t) = \left[\frac{k_1 \rho}{k_4 m \bar{P}_n(t)} \right]^{1/2} V(t), \tag{21}$$

and hence

$$\frac{dC}{dt} = k_2 \left[\left(\frac{k_1 m}{k_4 \rho} \right) \left(1 + \frac{\bar{P}_n(0) k_3 \rho C}{k_2 m} \right) \left(\frac{1-C}{\bar{P}_n(0)} \right) \right]^{1/2} \tag{22}$$

In figure 2 we see how eq (19) fits data available for polystyrene decomposition. Equation (22) also reproduces much of the rate of volatilization behavior of polystyrene. See figure 3 where we show the variation in the relative rate of volatilization

$$\frac{(dC/dt)}{(dC/dt)_{max}}$$ as a function of conversion, dashed

lines. The full lines are based on an equation, in which the square root is absent, devised by assuming termination to be monomolecular. Caged recombination would be one type of termination which is
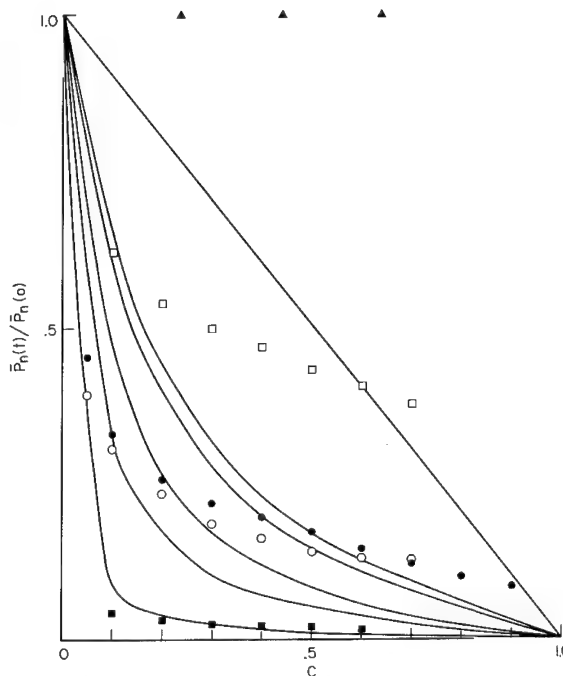

FIGURE 2. *Pyrolysis of polystyrene at 302 °C, relative number average degree of polymerization as a function of conversion.*

Full lines theory eq (19) numbers on curves equal values of factor $\left(\dfrac{P_n(0) K_3 \rho}{k_2 m} \right)$ in equation. The initial number average molecular weights, $M_n(0)$, are:
▲ 5,300   □ 37,000   ● 130,000   ○ 170,100   ■ 2 × 10⁶

kinetically monomolecular and may be involved in the degradation of polystyrene.

Study of the initial rates in the 0–0.03 conversion range of monodispersed or polydispersed volatilization reveals no correlation with the reciprocal of the molecular weight, i.e., number of ends and hence renders suspect that the mechanisms of initiation is at the molecular ends. The initial rates appear to be essentially independent of molecular weight.

The molecular weight distribution of degrading polystyrenes, both mono- and polydispersed, has been examined carefully [27] and found to approach the weight-to-number average DP ratio of 1.5 regardless of whether the initial ratio is one (fig. 4) or larger than two. This distribution is produced by pure coupling mechanisms. Statistically coupling of species in the "most probable" distribution produces narrower distributions [28, 29]. It would seem obvious that any random splitting into fragments followed by a statistical recoupling of the said fragments would approach a 1.5 weight-to-number average DP ratio, whatever the initial molecular weight distribution of the system. The mechanism of polystyrene decomposition continues to have many puzzling aspects. The mechanisms of initiation and termination are in doubt. The presence of a very short kinetic chain length and intermolecular transfer, however, is unquestionable.

6. Decomposition of Polytetrafluoroethylene

This polymer decomposes with a very short kinetic chain length, random initiation and termination by combination with perhaps a small amount of disproportionation occurring [30, 31]. In the treat-
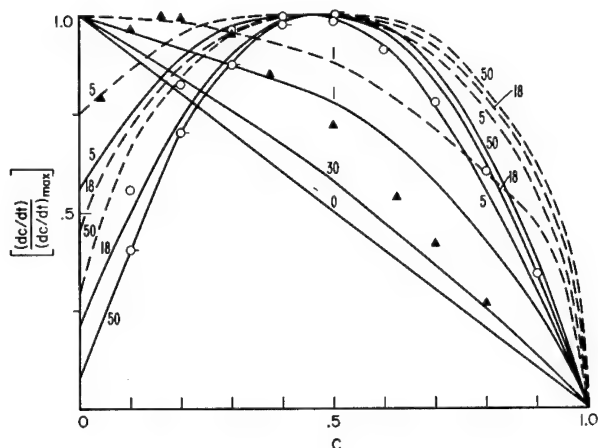

FIGURE 4. *Variation of the ratio of the weight to number average degrees of polymerization of polystyrene during thermalde gradation at 300 °C as a function of conversion.*

○ NBS 706 $P_n(0) = 1.31 \times 10^3$
□ NBS 705 $P_n(0) = 1.64 \times 10^3$
△ $\bar{P}_n(0) = 3.58 \times 10^2$

ment that follows, k_4 is the rate constant for total mutual termination, i.e., $k_4 = k_{4c} + k_{4d}$, where k_{4c} and k_{4d} are the rate constants for termination by combination and disproportionation, respectively. The steady state is then obtained by equating the rate of initiation to that for termination.

$$\frac{k_1 \rho V(t)}{m} = \frac{k_4}{V(t)} R(t)^2 \qquad (23)$$

$$R(t) = \left(\frac{k_1 \rho}{k_4 m}\right)^{1/2} V(t). \qquad (24)$$

Here, as before, $R(t)$ is the number of moles of radicals in a sample of weight, $\rho V(t)$. It is therefore not a concentration and the volume $V(t)$ comes into the second order rate expressions. The rate of conversion to volatile monomer is therefore given by

$$\frac{dC}{dt} = \frac{m d M}{w_0 dt} = \frac{m}{w_0} k_2 R(t), \qquad (25)$$

$$\frac{dC}{dt} = k_2 \left[\frac{k_1 m}{k_4 \rho}\right]^{1/2} (1 - C). \qquad (26)$$

In figure 5 we show some characteristic rate of volatilization curves for polytetrafluoroethylene which have the properties predicted by eq [26].

We now neglect the molecular vaporization of small polymer molecules. Then polymer molecules, Q, increase only by the disproportionation process.

FIGURE 3. *Pyrolysis of polystyrene, rates of volatizization as a function of conversion.*

Dashed lines theory bimolecular termination based on eq (22); full lines theory for monomolecular termination. Experimental data and theory all normalized so that $(dC/dt)_{max} = 1.0$. Experimental points:

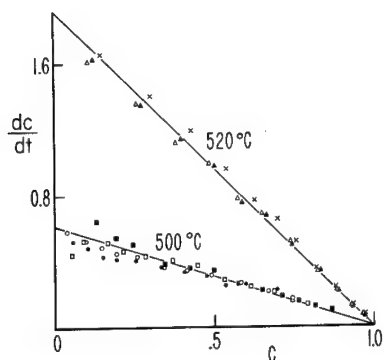|	$M_n(0)$	$T °C$
▲	5,300	343
○	170,100	331
○'	170,100	310

FIGURE 5. *Rate of depolymerization of polytetrafluoroethylene as a function of conversion.*

At 520°C the points are from three triplicate runs. At 500°C the points indicate results for samples with different prior dosages of gamma radiation.

Thus,

$$\frac{dQ}{dt} = \frac{k_{4d}R(t)^2}{V(t)}. \tag{27}$$

Combining eqs [25] and [27],

$$\frac{dQ}{dC} = \frac{k_{4d}}{mk_2}\frac{w_0 R(t)}{V(t)} = \frac{k_{4d}}{k_4}\frac{w_0}{m}\frac{1}{k_2}\left(\frac{k_1 k_4 \rho}{m}\right)^{1/2}. \tag{28}$$

The zip length, $Z = \dfrac{1}{2k_2}\left(\dfrac{k_1 k_4 \rho}{m}\right)^{-1/2}$. Integration of eq (28) gives

$$Q(t) - Q(0) = \frac{k_{4d}}{k_4}\frac{w_0}{m}\frac{C}{2Z}, \tag{29}$$

which becomes

$$\frac{w(0)(1-C)}{mP_n(t)} - \frac{w_0}{mP_n(0)} = \left(\frac{k_{4d}}{k_4}\right)\frac{w_0}{m}\frac{C}{2Z} \tag{30}$$

or

$$\frac{1-C}{\bar{P}_n(t)} - \frac{1}{\bar{P}_n(0)} = \left(\frac{k_{4d}}{k_4}\right)\frac{C}{2Z} \tag{31}$$

$$\text{valid for } Z \ll P_n$$
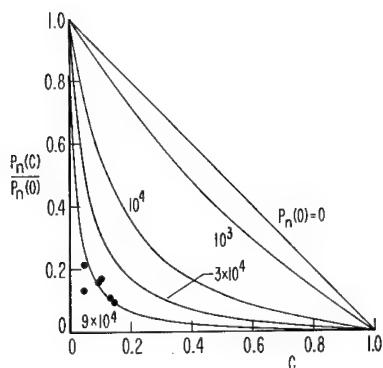
FIGURE 6. *Variation of relative degree of polymerization as a function of conversion.*

Points experiment at 480°C. Line theoretical from eq (32).

where P_n is the number average degree of polymerization.

Equation (31) may be rearranged to

$$\frac{\bar{P}_n(t)}{\bar{P}_n(0)} = \frac{(1-C)}{\left[1+\left(\dfrac{k_{4d}}{k_4}\dfrac{P_n(0)}{2Z}\right)C\right]}. \tag{32}$$

In figure 6 we show theoretical lines based on eq (32). Since we know the zip length [30], $Z=13$ at 480 °C, and the degree of polymerization initially and for degraded polymer [22] we find a value of ∼0.02 for $k_{4d}/(k_{4d}+k_{4c})$. The experimental observation can easily be due to organic impurities, thus, it is likely that termination in pure polytetrafluoroethylene would be entirely by combination.

7. Diffusion Effects Enhancing Rates of Initiation or Termination

During studies of the radiolytic depolymerization of polytetrafluoroethylene [30], it was observed that rates were enhanced as the samples were made thinner. The enhancement was also greater with greater dose-rates as shown in figure 7.
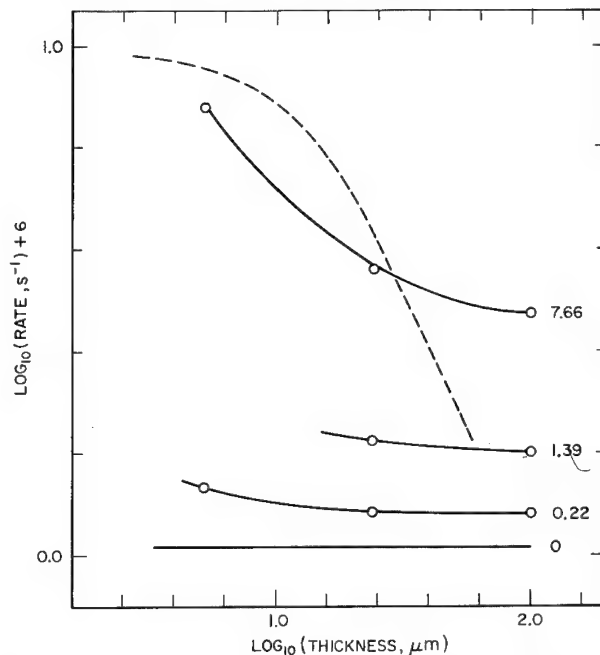
FIGURE 7. *Gamma ray induced depolymerization of polytetrafluoroethylene at —— °C.*

Full lines observed rates of monomer production as a function of sample thickness. Numbers to right of curves are dose rates, Mrad/hr. Dashed line is theoretical for back reaction of monomer. [30].

In large samples it is obvious that sample dimensions can influence the decomposition of polymers by way of retarded monomer escape, or of heat transfer restrictions. Some possible causes of sample size or surface influence have been put forward [32, 33, 34] in the past. The radiolytic depolymerization result is evidence of another mechanism for dimensional
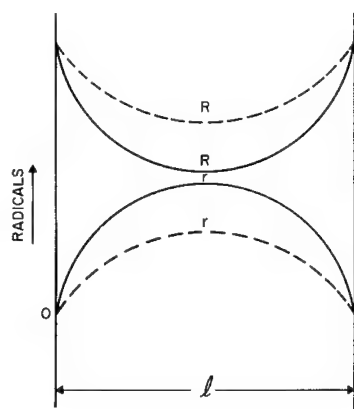
FIGURE 8. *Schematic drawing of the variation in the concentration of large, R, and small, r, radicals in an infinitely long slab of polymer having thickness l.*

For dashed curves, l is smaller than for full curves.

effects on rates which is operative at considerably smaller sample size, and which should be of general importance. The basic feature is that in cases where both large and small radicals or other small species participate in the reaction, the latter can escape at the surface, thus modifying the steady-state concentrations of all radicals in the shallower layers, and in particular that of the decomposing polymer radicals. In earlier studies of the trapping of small radicals at 4 K, it was observed that the radiolysis of solid methane produced methyl radicals and hydrogen atoms of different concentrations at long times [35].

A theoretical treatment [35] of this situation required consideration of the competitive diffusion of the two species. The specific process treated [35] is that of the radiation-induced decomposition of polytetrafluoroethylene at 400 to 450 °C.

It has been shown that the back reaction of monomer is inadequate to explain the observed trend of decomposition rate as a function of sample thickness [30]. Slow diffusion of the monomer through the sample has been considered over twenty years ago [29]. However, the variation of rate as a function of thickness was not calculated. The effect of introducing the back reaction,

$$R_i + M \xrightarrow{k_{-2}} R_{i+1},$$

into the usually depolymerization reaction as shown by the dashed curve in figure 7. It should also be pointed out that there is no effect in the pure thermal decomposition.
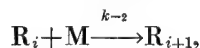
In figure 8 we schematically show the effect of a mechanism involving large polymer radicals, R, and small, r, on the concentration of R in a slab of infinite length. It is very clear that [R] and hence the rate of depolymerization increases the thinner the slab.

A survey of relative diffusion rates of polymeric molecules and small molecules, approximately 1 to 10×10^{-7} and 1×10^{-5} cm^2 s^{-1}, respectively, suggests

that it is permissible to ignore the migration of polymeric radicals. Relative termination rates are involved in the theory as well. Many of the known termination rate constants for small plus small and large plus large radicals are in the range 1 to 6×10^9 and 0.2 to 7×10^7 l mol^{-1} s^{-1}, respectively. It must be cautioned that all these values are for dilute solution near room temperature, while the medium under discussion here is molten polymer at several hundred degrees Celsius. Wider ranges of variation are suggested by values of diffusivity of small molecules in elastomers, of the order of 10^{-6} and 10^{-7} cm^2 s^{-1}, and by one termination constant 4.0×10^4 l mol^{-1} s^{-1} determined in a decomposing polymer melt. As a hypothesis concerning large plus small termination rates we rely on a formulation given originally in Smoluchowski's diffusion theory for spherical molecules, but often accepted in more complicated cases as well:

$$k_{12} = \frac{4\pi N_0}{1000} (D_1 + D_2) r_{12}. \qquad (33)$$

Here k_{12} represents the rate constant for the reaction of small with large molecules, N_0 is the Avogadro number, D_1 and D_2 are diffusivities, and r_{12} is the encounter distance in cm. Units of k_{12} are l mol^{-1} s^{-1}.

It is likely that for actual small molecules relative to large polymeric molecules, the encounter distances are essentially identical, and diffusivities are greatly different. Thus, setting $r_{12} = r_{11}$ and $D_2 \ll D_1$, it follows that:

$$k_{12} \cong \tfrac{1}{2} k_{11}, \qquad (34)$$

where k_{11} is the rate constant for reaction of two small molecules.

The above amounts to the estimate that large plus small termination rate constants are of the same order of magnitude as small plus small, and roughly about half as great. Polymeric radicals thus terminate with each other slowly, while small radicals terminate with each other or with large radicals much more rapidly. In layers near the surface, small radicals are depleted and only the slow termination of large plus large radicals remains. There is thus a high surface concentration of large radicals and a consequent high surface rate of decomposition. These considerations are embodied in the scheme below, where only random initiations are considered. Interesting special cases containing thermolytic end initiation can be developed, and at least one such will be mentioned later in this article.

Reaction	Rate
P→R	v_1, or $k_1\rho m + \Phi_1 I \rho/m$
P→S	v_2, or $\Phi_2 I \rho/m$
$R_{j+2} \rightarrow R_j +$ monomer	$k_2 R$
R+R→P	$k_4 R^2$
R+S→R−S	$k_5 RS$
S+S→products	$k_6 S^2$

Six reactions appear in the scheme, but the propagation, $k_2 R$, is involved only perfunctorily.
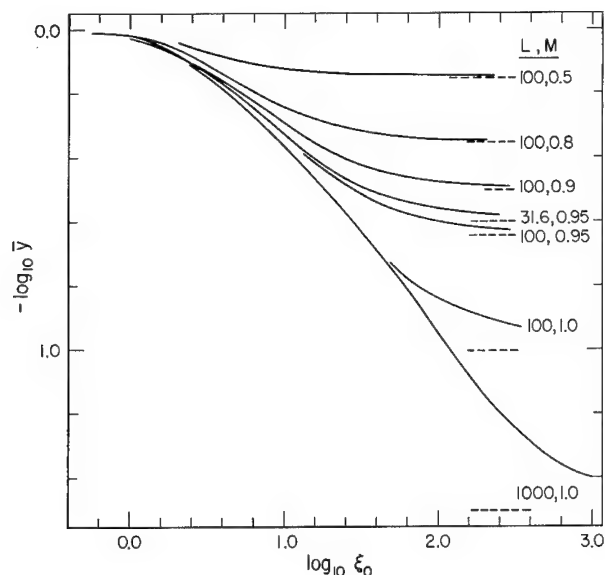
FIGURE 9. *Theoretical rates of monomer production as a function of sample thickness.*

Pairs of numbers at right are values for the parameters $L = k_5(k_4k_6)0^{1/2}$; $M = v_2/v_1$. The thickness parameter ξ_0 is the product of the actual thickness and the constant factor, $\left(\dfrac{2L}{D}\right)^{1/2} (v_1k_6)^{1/2}$, where D is the diffusion constant and v_1 the rate of production of large radicals. Horizontal dashed lines give limiting rate value, $\bar{y}$, at infinite thickness [31].

P, R, and S refer to polymer segments, polymer radicals and small radicals, respectively. The symbols v_1 and v_2 are radical generation rates; the alternative expressions given involve a random thermal initiation rate constant k_1, density ρ, segment molecular weight m, radiation dose rate I, and radiation efficiency factors Φ_1 and Φ_2. Because the small radical diffusivity D, cm^2 s^{-1}, will be used, concentration and rate-constant units are in moles, cm^3 and s.

We consider the time-independent steady state in a strip sample of thickness X cm with position-variable x cm below the free surface and an impermeable bottom. Evaporation of small radicals S keeps a surface concentration, $S=0$, at $x=0$. The steady state with diffusion is then

$$\frac{dS}{dt} = 0 = v_2 - k_6S^2 - k_5RS + D\frac{d^2S}{xx^2}, \qquad (35)$$

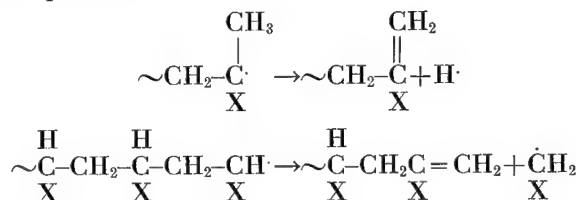$$\frac{dR}{dt} = 0 = v_1 - k_4R^2 - k_5RS. \qquad (36)$$

The solutions of the above equations are given elsewhere [31]. Figure 9 gives the same representative results graphically. Comparison of these with the experimental curves in figure 7 shows that the theory fits the main characteristics of the experimental observation.

It is at first surprising that the mechanism has a transition from thin-film to thick-film behavior at thicknesses much less than those involved in retarded monomer escape. The latter experimentally appears to cause no change of regime until thicknesses of tenths of a millimeter, under roughly comparable conditions. Superficially, this difference in location

of the transition region can be rationalized by noting that although the diffusivities, D, may be similar for monomer and small radicals, S, e.g., 10^{-5} cm^2 s^{-1}, the pertinent concentrations are very much smaller for the radicals. This suggests, by the inversion of Fick's first law, $(dC/dx) = (1/D)$ (flux rate), that at similar flux rates the radicals can go from near zero to near their maximum permissible concentration over a shorter interval. The full truth is not so simple, and would require comparison of generation and destruction rates as well. Although the treatment [31] was developed in order to elucidate γ-ray induced depolymerizations, it would be expected to apply to thermal depolymerizations initiated at the ends of polymer molecules depending on the size and diffusivity of the small radical produced.

Polystyrene [36] is thought to initiate with production of small radicals; however, it also has a very short kinetic chain length [37] and hence the effect would probably be very difficult to detect.

Essentially, the same mechanism can conceivably lead to slower rates with thinner films. Consider the following types of pseudo monomolecular termination processes:

$$\underset{\underset{\text{X}}{|}}{\overset{\overset{\text{CH}_3}{|}}{\sim\text{CH}_2-\text{C}\cdot}} \rightarrow \underset{\underset{\text{X}}{|}}{\overset{\overset{\text{CH}_2}{||}}{\sim\text{CH}_2-\text{C}}} + \text{H}\cdot$$

$$\underset{\underset{\text{X}}{|}}{\overset{\overset{\text{H}}{|}}{\sim\text{C}}}-\text{CH}_2-\underset{\underset{\text{X}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{CH}_2-\underset{\underset{\text{X}}{|}}{\overset{\overset{\text{H}}{|}}{\text{CH}\cdot}} \rightarrow \sim\underset{\underset{\text{X}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{CH}_2\text{C}=\text{CH}_2+\underset{\underset{\text{X}}{|}}{\overset{}{\dot{\text{C}}\text{H}_2}}$$

which would operate most efficiently at the surface of decomposing polymer melt or film. Thus, diffusion situations between large and small radicals or molecular species are likely to produce larger or smaller rates in thermolysis or radiolysis of small thin samples of polymeric materials.

However, when the modes of initiation and termination just discussed exist together and are equally affected by diffusion, the net result of changes in thickness is merely a change of kinetic chain length with no change in rate. To illustrate, let the steps be designated as follows:

Initiation

$$Q\overset{k_1}{\longrightarrow}R+S\uparrow$$

Propagation

$$R_{j+1}\overset{k_2}{\longrightarrow}R_j+M\uparrow$$

Termination

$$R\overset{k_4}{\longrightarrow}Q+S\uparrow$$
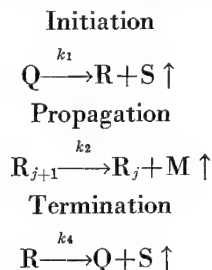
where Q, M, R, and S denote concentrations of polymer molecules, monomer, large radicals, and small radicals, and let the net effect of reduction in thickness be to double k_1 and k_4. Then the rate, dM/dt, is unchanged:

since, $$\frac{dM}{dt} = k_2\sum R_i = \frac{k_2k_1Q}{k_4},$$

56

while the kinetic chain length, z, is reduced to one half:

since,
$$z = \frac{k_2 R}{k_4 R} = \frac{k_2}{k_4}.$$

Some of these effects of thickness may have been encountered in other polymers. Films of polymethylmethacrylate have been reported to give higher rates [38] at such small thicknesses, 40 nm, that the mechanism treated here could be expected there as well. Their results in view of the high temperatures, short times, and procedures used, suggest in our opinion many other possible explanations.

Qualitatively, the interaction of large and small radicals at various depths could be important in still other reactions. The cosmic dust particles discussed by Donn [39], containing hydrocarbon and exposed to ultraviolet, are small enough, 1 to 10 nm thickness, so that efficient escape of H atoms would occur from a large portion or all of a particle. The radiation crosslinking of crystalline polyethylene is known to depend on thickness [40], as follows readily from our analysis if unescaped H atoms scavenge polymer radicals which would otherwise combine as crosslinks. The mechanistic consequences of diffusion and thickness would also be of obvious importance in oxidative degradation.

8. Diffusion and the Cage Effect

In a relatively few cases only, have values for the activation energy for initiation and other elementary steps been deduced in polymer depolymerizations. The rates of elementary processes in polytetrafluoroethylene decomposition [30] are:

Initiation $\quad k_1 = 2.1 \times 10^{28} e^{-118,600/RT}$ s^{-1}

Propagation $\quad k_2 = 7 \times 10^{11} e^{-36,200/RT}$ s^{-1}

Termination $\quad k_4 = 3 \times 10^{13} e^{-30,000/RT}$ l m^{-1} s^{-1}.

In the depolymerization of polymethylmethacrylate [44] it appears that

$$k_4 = 3 \times 10^{14} e^{-20,000/RT}.$$

For poly-α-methylstyrene [43],

$$k_1 = 4 \times 10^{18} e^{-65,000/RT}.$$

In table 4 we present the A-factors and activation energies for the overall rate of decomposition (volatilization) of several polymers. Very high A-factors are evident for these systems. In two cases,

TABLE 4. *Preexponential factors and activation energies for the thermal decomposition of polymers* [45]

Polymer	A, s^{-1}	E, kcal/m
α-methyl styrene	10^{22}	65
tetrafluoroethylene	10^{19}	81
$\alpha\beta\beta$-trifluorostyrene	10^{19}	64
ethylene (linear)	10^{18}	72
methyl methacrylate	10^9–10^{16}	30–52
styrene	10^{15}	55

it is indicated that the A-factor for the initiation process is very high. It is likely that in the other cases the initiation step has high A-values and hence A-values for the net processes are high.

Since the early work of Cowley and Melville [44], it has been known that the mutual termination of radicals in pyrolyzing melts is diffusion controlled and the rates of termination have experimentally large (≥ 20) activation energies. In the case of polytetrafluoroethylene the activation energy and A-value for initiation also demonstrate that the effect of diffusion (cage effect) must be considered when discussing organic mechanisms in hot melts. It has been pointed out [45] that in the melt the dissociation energy of a bond in the interior of a large polymer molecule would be the difference of the activation energies for initiation and termination: $D(R-R)_m = E_1 - E_4$. In the gas phase $E_4 = 0$, hence, $D(R-R)_g = E_1(\text{gas})$. For polytetrafluoroethylene, then the activation energy to produce active radicals is $D(R-R)_m + E_4 = 118.6$ using the data above. The concomitant high A-values indicate a highly disordered transition state which must encompass $\sim$5–10 CF$_2$ units. Numerically, it requires $\Delta S\ddagger$ equivalent to the vaporization of ≥ 10 CF$_2$ units.

These results and conclusions raise certain questions concerning the relationship between the dissociation energy in the melt, $D(R-R)_m$ and that in the gas phase $D(R-R)_g$. Of course, since these large molecules cannot really vaporize, the latter quantity is for an idealized process. Considering the cycle:
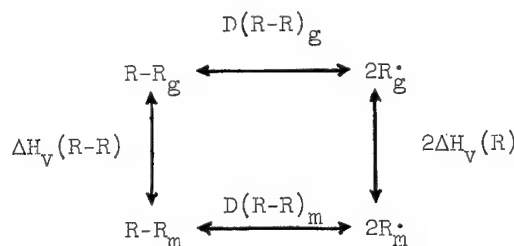
If, as might be reasonable, we assume: $D(R-R)_m \equiv D(R-R)_g$, then, $\Delta H_v(R-R) \equiv 2\Delta H_v(R)$. This would be a very useful situation but we reject it because at least in the case of the n-alkanes it is not compatible with known data, see eq (8). From the above cycle we can derive the relation for dissociation of the central interior bond in a large n-alkane molecule.

$D(R-R)_g$
$$= D(R-R)_m + 2\Delta H_v(R-) - \Delta H_v(R-R).$$

From eq (8) it follows: $D(R-R)_g = D(R-R)_m + 0.26(3.21 n^{2/3}) - 0.0193T + 2.92$. Here, n is the number of carbon atoms in $R-R$, the original molecule. For a large linear n-alkane of 1000 carbon atoms we find that at 27 °C, $D(R-R)_g = D(R-R)_m + 80.59$ kcal.

One concludes from the above result that the "true or ideal" dissociation energy for large molecules

TABLE 5. *Zip lengths for polymer depolymerization at 1 percent/min rates*

Polymer	Zip lengths
methyl methacrylate	$\sim 10^3$
α-methyl styrene	$\sim 10^3$
styrene	~ 5
tetrafluoroethylene	~ 3

should come from measurements in the melt phase or more precisely in a theta condition [46]. This follows since it seems clear that $D(\text{R}-\text{R})_m$ is the energy characteristic of the chemical bond. One suspects that there may be an appreciable activation energy for recombination of large molecules in the gas phase, since in the formation of the big molecules a certain amount of reorganization would occur.

9. Thermodynamics of Polymer Decomposition

The decomposition of organic polymers is, in general, more a function of the dissociation rates of bonds in the molecular structure, rather than the thermodynamic properties of the material, since photo and gamma rays will often initiate rapid decomposition of some polymers at certain temperatures. Such effects will occur more strongly the longer the zip length of the polymer decomposition mechanism.

$$\text{Zip length} = \frac{\text{Depropagation to Monomer}}{\text{Termination} + \text{Transfer}}$$

TABLE 6. *Thermodynamic quantities for decomposition of polyethylene and polytetrafluoroethylene.*

	ΔH kcal/mole	ΔS kcal/mole	ΔF kcal/mole
$\sim CH_2CH_2\sim \overset{a}{\rightarrow} CH_2CH_2$	22.35	34.07	12.19
$\overset{b}{\rightarrow} 1/3 C_6H_6 - H_2$	16.46	34.28	6.23
$\overset{c}{\rightarrow} 2C(\text{Graphite}) - 2H_2$	9.85	46.76	+4.10
$\overset{d}{\rightarrow} n\text{-Alkenes} [(1/18)CH_3 (CH_2)_{33}CH = CH_2]$	1.09	2.03	0.49
$\overset{e}{\rightarrow} C(\text{Graphite}) - CH_4$	−8.04	27.49	+16.23
$\sim CF_2CF_2\sim \overset{f}{\rightarrow} CF_2CF_2$	46	45	33
$\overset{g}{\rightarrow} 2C(\text{Graphite}) - 2F_2$	194	71	172
$\overset{h}{\rightarrow} C(\text{Graphite}) - CF_4$	−27	35	+38

* With the exception of graphite all the substances are taken to be in the "ideal" gas state at 298.2 K. For the high polymers this "ideal" gas state is evidently for the polymer in its most extended conformation [5].

TABLE 7. *Comparison of decomposition and ceiling temperature*

Polymer	T_d ,C	T_c ,C
Tetrafluoroethylene	510	680
Ethylene	410	400
Propylene	380	300
Styrene	360	230
Methyl methacrylate	330	220
Methacrylonitrile	250	177
Isobutylene	340	50
α-methyl styrene	290	7
Formaldehyde	120	35

That is, the average number of monomer units produced by a decomposing radical before the radical is deactivated either by termination or transfer. See table 5 where some estimated zip lengths are listed.

Consideration of table 6, which gives values of the various thermodynamic functions for the decomposition of polyethylene and polytetrafluoroethylene by several different processes into quite different products, illustrates how metastable organic polymers are. It is interesting to note that certain of the conceivable mechanisms are very exothermic, but that the polymers normally decompose by reactions which are not thermodynamically favored at ambient temperatures. It would seem that the possibilities for the incorporation of catalyst for controlling the decomposition of polymers to give non-combustible volatiles could be extensive.

Polymers are then in general metastable. We see this fact also in table 7. Most polymers listed show greater stability than one would expect from their ceiling temperature T_c. This is the temperature where the rate of propagation equals the rate of depropagation or the equilibrium constant for the reaction, $R_i + M \rightleftarrows R_{i+1}$, equals one. Thermodynami-
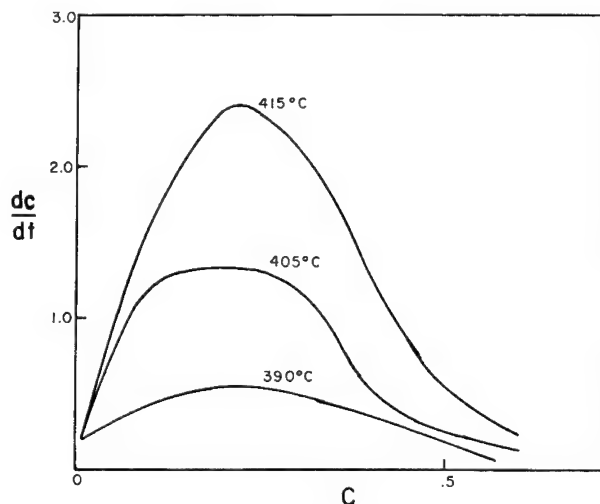

FIGURE 10. *Pyrolysis of polycarbonate, rates of volatilization as a function of conversion, activation energy based on maximum rates, 53 kcal/mole.*

cally then, polymers can decompose above T_c, which can be estimated from the following relation:

$$T_c = \frac{\Delta H^0_p}{\Delta S^0_p}$$

where the quantities ΔH^0_P and ΔS^0_P refer to the standard enthalpy and entropy of polymerization.

10. Aromatic Polymers

Aromatic polymers, such as polycarbonate, polymellitimide and polydimethylphenyleneoxide, tend to decompose in varying degrees to a char, i.e., a carbonaceous residue. Most of these polymers are insoluble and hence study of the decomposition processes, particularly those producing crosslinks or scission is extremely difficult if not impossible. One polymer that is soluble is the polycarbonate which dissolves in dioxane.

On pyrolysis, polycarbonate [47] volatilizes rapidly at first but quickly drops to a very slow rate in the vicinity of 0.50 conversion (see fig. 10). At this stage ~0.50 conversion, the residue is a carbonaceous char.

At lower temperatures ~300°, it is found that the percent gel in the polymer increases with conversion to values of ~90 percent at ~10–20 percent conversion. The swelling ratio of the gel decreases with the conversion, but less strongly the higher the temperature. These observations indicate a competition between net scission and crosslinking processes as a function of conversion. The relative ratio of the two depends on temperature, the thickness of the sample and also on the amount of oxygen present. In figure 11 we show the effect of thickness and air. The thicker the polymer the slower the rate at the longer times. These curves also suggest that the thicker samples as might be expected favor crosslinking. In figure 12 we compare the rates of volatilization at 410 °C of various samples preheated
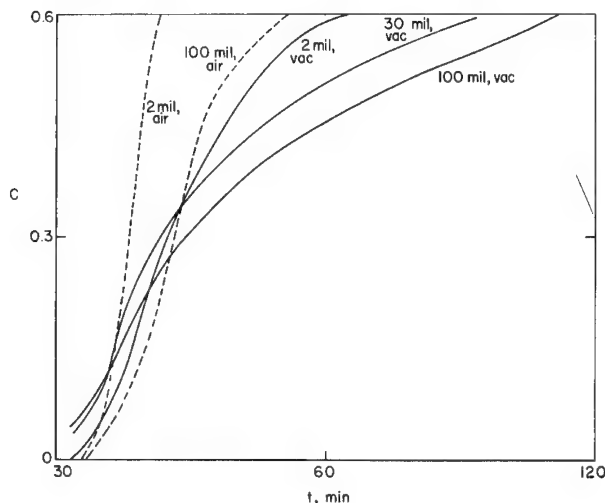

FIGURE 12. *Pyrolysis of polycarbonate at 410 °C.*

Effect of preheating at 315 °C on rates as a function of conversion. Numbers in curves give percent weight loss during the preheat period.

at 315 °C to the percent weight losses indicated by the numbers on the curve. The conclusion is that the greater the crosslinking the less the rate of volatilization. Thus, the aromatic chain polymers, in that they tend to crosslink and eventually char, are mechanistically different from the saturated line polymers where scission processes predominate. As yet the understanding of the degradative process in aromatic polymers is so limited that theoretical developments are not feasible.

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FIGURE 11. *Pyrolysis of polycarbonate, effect of thickness on conversion as a function of time.*

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Discussion

W. Tsang (National Bureau of Standards):

In the decomposition of medium sized (C_5 or above) olefinic and acetylenic compounds in a single pulse shock tube at about 1100 K, concurrent with the bond breaking processes, there appears to be a molecular process of the type observed by Bailey [W. J. Bailey, SPE Trans. **5**, 1 (1965)]. For the acetylenic compound 4-methylpentyne-1 the rate expression for the molecular process is [W. Tsang, Int. J. Chem. Kinetics **2**, 23 (1970)]

$$k(\text{4-methylpentyne-1} \rightarrow \text{allene} + \text{propylene})$$

$$= 10^{13.1} \exp(-58,500/RT) \text{ s}^{-1}.$$

Furthermore, it appears that the molecular reaction for olefin decomposition follows a similar expression. On the other hand, for the cleavage of a normal alkane, the shock tube data suggest a rate expression of the form $k[n\text{-alkane} \rightarrow (\text{Radical})_1 + (\text{Radical})_2] \sim 10^{16.3} \exp(-82,000/RT) \text{ s}^{-1}$. If such data are applicable to the pyrolysis of polyethylene or any other polyolefin at 700 K, it would appear that unless unsaturated impurities are less than 1 part in 100,000, the initial degradation process must also involve a molecular reaction.

Leo A. Wall:

Reactions of unsaturated substances of the type that Dr. Tsang calls to our attention may be occurring in the pyrolysis of polyethylene; however, experimental evidence indicates they are of negligible importance. During the thermal degradation of polyethylene vinyl end groups are produced (Oakes and Richards, J. Chem. Soc. 2929 (1949)) by a random cleavage reaction which has the rate constant $10^{17.6}e^{-72,000/RT}$, (S. Straus and L. A. Wall, J. Res. NBS **65A**, 221 (1961) deduced from the maximum rate that occurs in the vicinity of 26 percent weight loss. From the thermal stress relaxation of crosslinked polyethylene in the vicinity of ≤ 1 percent weight loss, a similar value, $10^{20}e^{-73,000/RT}$, for the cleavage process is deduced.

One of the still to be determined questions about the mechanism of the thermal decomposition reaction of polyethylene between 300–450 °C is whether this cleavage process is or is not a chain reaction. If it is, then it would appear that polyethylene decomposition is initiated by the dissociation of carbon-carbon bonds.

Patterns and Problems in the Pyrolysis Behaviour of Synthetic Addition Polymers

G. G. Cameron

University of Aberdeen, Aberdeen, Scotland

The types of pyrolytic decomposition reactions undergone by synthetic addition polymers are outlined. Particular attention is given to two classes of polymer—those which undergo unzipping to monomer and those which fragment randomly along the backbone to yield low polymer. Free radical transfer reactions, usually involving tertiary hydrogen atoms, can play an important part in these degradation reactions. The thermal stability of addition polymers is not always predictable from known reactions of small molecules. This is often due to the presence of labile irregularities which are chemically incorporated in the macromolecules and which can initiate thermal decomposition. Also, since polymers are susceptible to chain reactions and neighbouring group effects, these abnormalities can affect the stability of a large proportion of the sample. The effects on pyrolysis of abnormalities such as unsaturation, chain branches, head-to-head links and oxidation products are discussed.

Key words: Free radicals; polymer abnormalities; polymer degradation; polymer pyrolysis; transfer reactions.

1. Patterns of Decomposition

The vacuum pyrolysis of addition polymers has been the subject of many detailed studies during the past twenty years. Consequently it is now possible to make certain generalizations regarding the link between structure and decomposition mechanism. Most of the polymers considered here can be represented by the generalized structure—

$$\left[CH_2-\underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{C}} \right]_n$$
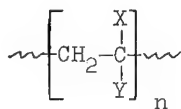
which shows the repeat unit of the initial monomer

$$CH_2 = \underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{C}} \; .$$
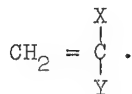
The pendant groups, X and Y, may be hydrogen or some other substituent such as a halogen, nitrile group, etc. Three distinct types of degradation reaction can occur with such polymers: (a) depolymerization to yield monomer; (b) random breaking of the polymer backbone to yield small polymer fragments; (c) reactions involving substituents X and Y.

Polymers in categories (a) and (b) can usually be converted completely to volatile materials, while those in (c) generally form a char or residue. While some polymers have degradation patterns which fit almost exclusively into one of these categories many show intermediate behaviour. For example, poly(methyl methacrylate) gives $\sim$98 percent monomer on pyrolysis and therefore falls into category (a), but polystyrene gives a mixture of monomer ($\sim$45 percent by wt.) and low polymer and therefore shows characteristics of both (a) and (b). Poly(methyl acrylate) yields low polymer fragments as well as CO_2 and methanol so that it shows characteristics of (b) and (c). A few polymers also crosslink during pyrolysis. Table 1 shows a list of some addition polymers in categories (a) and (b) with the monomer yield on pyrolysis.

This table highlights behavioural patterns. When neither X nor Y are hydrogen atoms, yields of monomer are very high. When X is replaced by a hydrogen atom there is a dramatic fall in monomer yield (compare poly(methyl methacrylate) with poly(methyl acrylate) and polymethacrylonitrile with polyacrylonitrile). Similarly among the polystyrene-types, replacement of the α-hydrogen atom, even by deuterium, increases the monomer yield. Clearly the α-hydrogen atoms play a key role in the decomposition pattern. This fact can be rationalized to a large extent if we assume that decomposition involves a free radical chain reaction. This assumption has been shown to be valid in a number of systems and it is reasonable to extend it to others showing similar behaviour.

TABLE 1. *Yields of monomer on pyrolysis of some addition polymers and transfer constants of polymer radicals to toluene at 60°C*

Polymer	X	and	Y in $-CH_2-\underset{\underset{Y}{\overset{\overset{X}{|}}{|}}{C}-$	Monomer yield Wt. %	K_{trans} to toluene
Poly(methyl methacrylate)	CH_3		CO_2CH_3	>98	1.25×10^{-2}
Poly(methyl atropate)	C_6H_5		CO_2CH_3	>99	—
Polymethacrylonitrile	CH_3		CN	90	2.00×10^{-2}
Poly(methyl acrylate)	H		CO_2CH_3	trace	0.56
Polyacrylonitrile	H		CN	5	0.79
Polyethylene	H		H	0	—
Polypropylene	H		CH_3	2	—
Polystyrene	H		C_6H_5	45	2.11×10^{-3}
Poly(α-methyl styrene)	CH_3		C_6H_5	95	—
Poly(α-deuterostyrene)	D		C_6H_5	70	—
Poly(β-deuterostyrene)	H		C_6H_5	42	—

The α-hydrogen atoms can take part in transfer reactions of the type:

$$\tag{1}$$
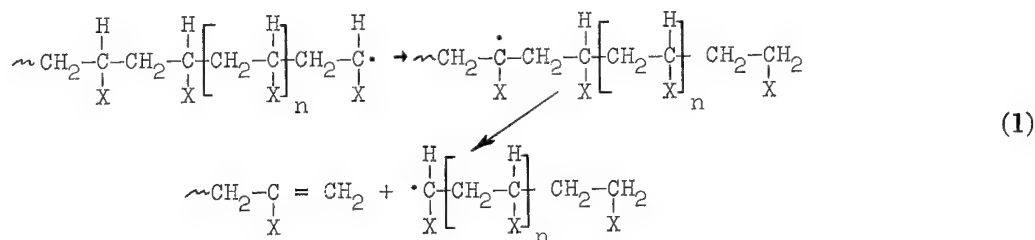
which shift the radical centre from a chain end (the propagating radical) to an intrachain position. Scission at the new radical centre leads to fragmentation of the original polymer chain. Such transfer reactions may be *intra*molecular (to a hydrogen atom on the same chain) or *inter*molecular (to a hydrogen atom on another chain). When α-hydrogen atoms are replaced by methyl or other groups transfer reactions are less favoured and an unzipping or reverse polymerization process takes over, leading to monomer as a major degradation product. This explains the marked difference in behaviour of poly(methyl methacrylate) and poly(methyl acrylate) for example.

Ready availability of α-hydrogen atoms is not, however, the only criterion in determining the course of decomposition, otherwise we should expect polystyrene to produce little, if any, monomer. Another factor which must be taken into account is the reactivity of the propagating radical as a transferring species. On this basis the relative transfer constants for a series of polymer radicals measured under identical conditions should follow a pattern similar to that observed for the yield of monomer on thermal degradation. Such a set of transfer constants of several polymer radicals towards toluene [1][1] at

60° is also shown in table 1. Correlation is fairly good. Polymer radicals with low values of K_{trans} give high yields of monomer and vice versa. The polystyryl radical does not transfer very frequently, despite the abundance of α-hydrogen atoms, because it is relatively unreactive. This is presumably a consequence of the stabilizing influence of the benzene ring. These generalizations, though rather oversimplified, provide a convenient framework for considering the overall pyrolysis behaviour of polymers in categories (a) and (b).

It should be made clear that while free radical intermediates are involved in most unzipping and random fragmentation reactions it is by no means certain that this generalization can be applied to all thermal degradations, particularly those involving side chain decomposition.

2. Factors Affecting Thermal Stability of Polymers

The thermal decomposition reactions of polymers are not always predictable from known reactions of small molecules. This is often due to the macromolecular nature of the reacting species in which the decomposition of one unit in the chain can activate the decomposition of an adjacent unit. For example, in the deacetylation of poly(vinyl acetate)

once the first molecule of acetic acid has been eliminated the double bond formed in the backbone weakens the next ester group and facilitates further reaction resulting in long sequences of conjugated double bonds [2].

The unzipping process, which produces monomer, may occur more rapidly and at much lower temperatures than a model reaction. Thus poly(ethyl methacrylate) liberates monomer in high yield at about 250 °C while primary ethyl esters are stable at this temperature and eventually decompose into ethylene and carboxylic acid at about 450 °C.

In the case of the polyolefins thermal decomposition occurs as in model short-chain paraffins. Polyethylene yields shorter chain monoolefins. However, significant decomposition occurs some 100 °C below that observed in the model. A similar effect is observed with poly(vinyl chloride) which decomposes by loss of HCl leaving an olefinic residue. This reaction is in accord with predictions from simple chloroparaffins but again occurs at a much lower temperature than predicted by the model. Effects of this type are by no means rare and can often be attributed to the presence of labile irregularities in the polymer chains. These abnormal structures can be formed during or after polymerization and are partly responsible for the varying thermal stabilities of different samples of the same polymer.

From a technical point of view it is obviously desirable to improve, as far as possible, the thermal stability of polymeric materials. It is therefore pertinent to consider how thermolabile irregularities are incorporated into the polymer structure and how they can affect degradation reactions. It is important at this point to distinguish clearly between irregular structures chemically bonded to the polymer chains and adventitious contaminants physically mixed with the polymer. In this article we are concerned only with the former. However, there are many examples in the literature of the destabilizing effects of impurities, particularly residues of polymerization initiators. The doubtful purity of many polymer samples studied in the past is probably responsible for much of the conflicting data which has appeared in the literature.

Some examples of chemically bonded abnormalities, incorporated both during polymerization and as a consequence of post-polymerization treatment, and their behaviour on pyrolysis are discussed in more detail below. The list is illustrative rather than exhaustive and raises a number of contentious points.

2.1. Unsaturation

One of the earliest studies on polymer degradation concerned poly(methyl methacrylate). This work established that there are at least two initiation reactions which can lead to unzipping of this polymer to monomer [3]. In samples prepared by free radical routes it was shown that approximately half of the polymer chains could be decomposed at temperatures about 220°C while the remainder required to be heated to 270 °C before significant decomposition

occurred. During free radical polymerization of methyl methacrylate termination is mainly by disproportionation—

(A)

$$(2)$$
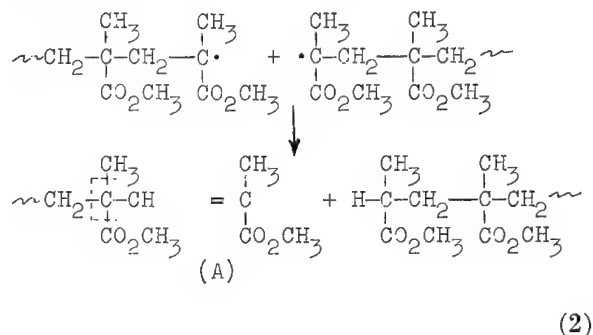
leading to about 50 percent of polymer chains with unsaturated end groups, the remainder being wholly saturated. It was proposed that the unsaturated groups constituted weak spots in the chains and were responsible for the low temperature reaction by facilitating scission at one of the bonds indicated to form an allylic radical. The kinetics of the low temperature reaction were found to be consistent with a chain-end initiated reaction.

More recently it has been shown that the unsaturated end formed by disproportionation has the structure
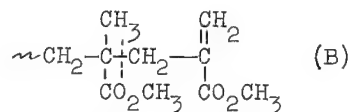
which leads directly to the depropagating radical
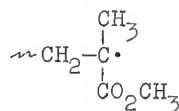
on decomposition. This destabilizing abnormality is a consequence of the polymerization mechanism and is difficult to eliminate in free radical polymerizations. Poly(methyl methacrylate) polymerized anionically contains no unsaturation and is noticeably more thermostable than its free radical counterpart undergoing depolymerization after high temperature initiation.

The high temperature reaction appears to occur by random homolytic scission.

(C)

$$(3)$$
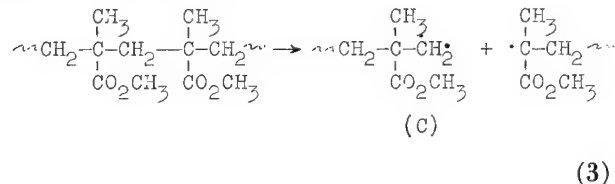
It is normally assumed that both radicals are capable of unzipping to monomer and certainly the available evidence suggests that if the initial polymer chains are short enough they are completely converted to

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monomer once initiated. The two radicals produced in this manner must have very different reactivities and in view of the earlier comments it is possible that the radical (C) undergoes some rapid reaction besides unzipping. Photolysis of poly(methyl methacrylate) also produces random homolytic scission, but E.S.R. examination of the degraded glasses shows no evidence of radical (C) [4]. The spectrum of the propagating radical can be identified along with a weaker four-line spectrum which has been attributed to an allylic radical formed from (C) as follows:

$$\sim CH_2-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\dot{C}H_2 \rightarrow \sim \dot{C}H-\overset{\overset{CH_3}{|}}{C} = CH_2 + HCO_2CH_3$$

(C)   (4)
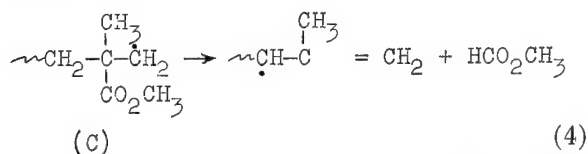
It is possible that during thermal degradation radical (C) reacts in a similar fashion, e.g.,

$$\sim CH_2-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\dot{C}H_2 \longrightarrow \sim CH_2-\overset{\overset{CH_3}{|}}{C} = CH_2 + \cdot CO_2CH_3$$

(D)   (5)

The structure (D) would constitute a thermolabile group which could lead to an element of chain-end initiation superimposed on the random kinetics. A similar conclusion has been reached on the basis that radical (C) would transfer rather than unzip [5].

When the polymer chains are long cf. the zip length a bimolecular termination step occurs. If this step is by disproportionation, as in polymerization, unsaturated end groups of type (B) are formed.
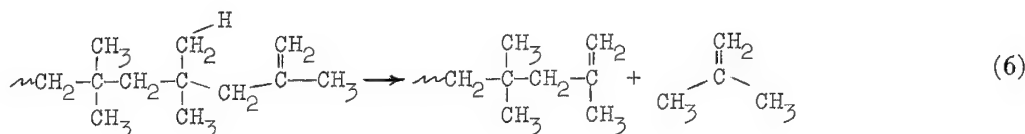
The partially degraded polymer is therefore less stable than the original and the kinetics of degradation are complicated by an element of chain-end initiation superimposed on the original random process. A reexamination of some earlier rate data for poly(methyl methacrylate) bears out this comment and shows that the kinetics and mechanism of the randomly initiated depolymerization are more complicated than is commonly supposed [6]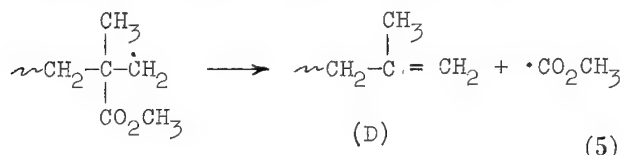. In the structurally similar polymer, poly(methyl atropate), random initiation of unzipping occurs in the early stages of pyrolysis but beyond about 45 percent conversion chain-end initiation predominates [7]. The accumulation of labile chain ends as discussed above may account for this.

The above discussion shows how a thermolabile unsaturated end group may be formed in a previously saturated macromolecule as a consequence of thermal degradation. Similar structures could be formed by any process which leads to chain scission, e.g., mechanical degradation or exposure to radiation. The latter processes may be carried out below the ceiling temperature of the polymer without evolving monomer and provide examples of abnormalities introduced by post-polymerization treatment.

Unsaturated chain ends are likely to be a source of weakness in any polymer system but do not necessarily initiate depolymerization via a radical chain mechanism. In the case of polyisobutylene random degradation occurs and appreciable quantities of monomer appear in the volatile products. Some of this monomer is almost certainly produced via free radical intermediates, but it has been shown by deuterium labelling studies that unsaturated end groups (formed in proton expulsion termination of polymerization) can evolve monomer via a cyclic mechanism [8].

$$\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{||}}{C}} \overset{H}{\underset{CH_2}{\diagdown}} \overset{CH_2}{\underset{||}{C}}-CH_3 \longrightarrow \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{||}}{C}} + \underset{CH_3}{\diagup}\overset{\overset{CH_2}{||}}{C}\underset{CH_3}{\diagdown} \qquad (6)$$

Any unsaturation produced by a scission reaction would behave in a similar manner. The effects of unsaturation on the decomposition of other polymeric hydrocarbons has been studied by Bailey [8].
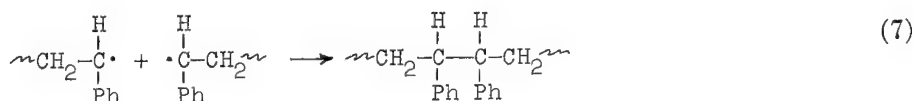
Unsaturation within the main chain can also occur in certain polymers. McNeill and coworkers

found that polystyrene prepared by a free radical route contains about 1.5 double bonds per 1000 monomer units [9]. No terminal unsaturation was present when benzoyl peroxide was used as initiator. This is consistent with the fact that, unlike the case of methyl methacrylate, termination in styrene polymerization is predominantly by combination.

$$\sim CH_2-\underset{\underset{Ph}{|}}{\overset{\overset{H}{|}}{C}}\cdot + \cdot\underset{\underset{Ph}{|}}{\overset{\overset{H}{|}}{C}}-CH_2\sim \longrightarrow \sim CH_2-\underset{\underset{Ph}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Ph}{|}}{\overset{\overset{H}{|}}{C}}-CH_2\sim \qquad (7)$$
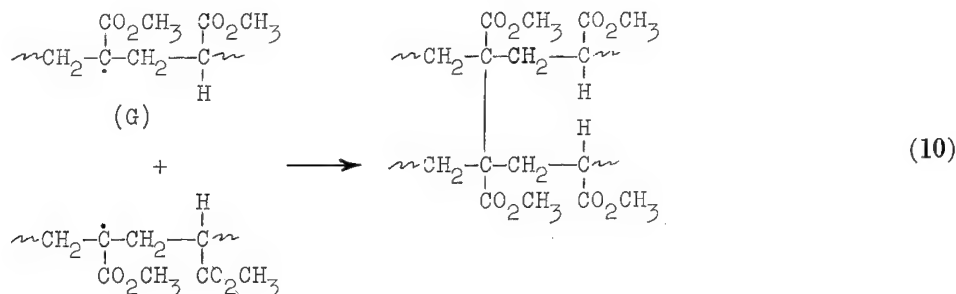
(The effect of the resulting head-to-head structure is considered later). The source of main chain unsaturation in free radical polystyrene is obscure but

McNeill has suggested [9] that it could arise from transfer to polymer:

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$$\text{\Large \textasciitilde CH}_2\text{--}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}\text{--CH}_2\text{--}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}\text{--CH}_2\text{\textasciitilde} + \text{R}\cdot \longrightarrow \text{RH} + \text{\textasciitilde CH}_2\text{--}\overset{\displaystyle \cdot}{\underset{\underset{\displaystyle Ph}{|}}{C}}\text{--CH}_2\text{--}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}\text{--CH}_2\text{\textasciitilde}$$

(E)

$$\downarrow$$

$$\text{\textasciitilde CH}_2\text{--}\underset{\underset{\displaystyle Ph}{|}}{C} = \text{CH--}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}\text{--CH}_2\text{\textasciitilde} + \text{H}\cdot$$

(8)

The radical (E) could reinitiate polymerization giving rise to a branch, or the adjacent methylene group could eliminate a hydrogen atom to form a double bond as in (F). The bonds indicated in structure (F) would be weakened compared with normal backbone bonds. If this mechanism of double bond formation is correct, then unsaturation in the backbone should increase with conversion during polymerization. Consequently polystyrene samples prepared to high conversion should be less thermally stable than low conversion polymers. This has been shown to be the case in pyrolysis studies of polystyrenes prepared under different conditions [10]. In this work the degradation temperature was kept below the ceiling temperature so that bond scission could be studied without the complication of significant formation of volatiles. Figure 1 shows plots of the fraction of bonds broken (α) as a function of time of heating at 287° for two samples of poly-

FIGURE 1. *Degree of degradation, α, versus time of heating at 287°.*

$\triangle$ = TPS/5 (12.5 percent conv.)
$\odot$ = TPS/6 (60 percent conv.)

styrene prepared under identical conditions except that the conversions of monomer to polymer for TPS/5 and TPS/6 were 12.5 and 60 percent respectively. The high conversion polymer, TPS/6, is markedly more thermolabile. This evidence is not unequivocal proof that TPS/6 contains more unsaturation than TPS/5. An increase in concentration of any abnormality could bring about the same effect. However, branching is the only other abnormality which would be expected to be conversion dependent but from a knowledge of the likely branch density the authors concluded that increased unsaturation was a more acceptable explanation. The activation energy for random bond scission in free radical polystyrene lies in the range 49–54 kcal mole^{-1} which is some 15–20 kcal lower than the estimated bond dissociation energy of normal backbone bonds. Unsaturation, as in structure (F), would lower the bond energy of the β C—C bonds by about 17 kcal. Thus, a contribution to degradation by decomposition at double bonds is consistent with the measured activation energy. Polystyrenes prepared by anionic routes are more thermostable than free radical polymers and have activation energies for random scission in the region of 70 kcal [11]. Propagation in anionic polymerization seems to be comparatively free from abnormal steps and termination, normally by proton addition, yields a more stable end structure. In the case of cationic polymerization of styrene proton expulsion leads to unsaturated chain ends but no main chain unsaturation [12]. The effects of these unsaturated ends has not been investigated in detail but would be expected to destabilize the polymer.

2.2. Branching

Chain branches on polymers normally arise by transfer to polymer during free radical polymerization. Transfer may be intermolecular yielding long branches. Short-chain branches may be formed by intramolecular transfer, a process which is apparently relatively frequent during the high pressure polymerization of ethylene.

(9)

High pressure polyethylene is characterized by the frequency of these short branches. The precise effect of branches on the thermal stability of high pressure polyethylene is not absolutely clear since other abnormalities, mainly oxygenated groups, are generally present also. It has been suggested that branching introduces more intramolecular transfer at the expense of intermolecular transfer due to the more compact form of highly branched molecules, particularly when the branches are long [13, 14].

Branched structures also occur during free radical polymerization of poly(methyl acrylate), probably by transfer to the relatively labile α-hydrogen atoms. The effect of branches on the pyrolysis behaviour of this polymer is rather different from that operating in polyethylene. Many features of the degradation of poly(methyl acrylate) are unusual; among these is the formation of appreciable quantities of insoluble gel in the polymeric residue [15, 16]. Gel formation is a consequence of some crosslinking reaction which may be a combination of radicals.

$$
\begin{array}{c}
\quad\quad CO_2CH_3 \quad CO_2CH_3 \\
\sim CH_2-\overset{\bullet}{\underset{\quad}{C}}-CH_2-\overset{}{\underset{H}{C}}\sim \\
(G) \\
+ \\
\quad\quad\quad H \\
\sim CH_2-\overset{\bullet}{\underset{\quad}{C}}-CH_2-\overset{}{\underset{}{C}}\sim \\
\quad\quad CO_2CH_3 \quad CC_2CH_3
\end{array}
\quad\longrightarrow\quad
\begin{array}{c}
\quad CO_2CH_3 \quad CO_2CH_3 \\
\sim CH_2-\overset{}{\underset{|}{C}}-CH_2-\overset{}{\underset{H}{C}}\sim \\
\quad | \quad\quad\quad | \\
\quad\quad\quad\quad\quad H \\
\sim CH_2-\overset{}{\underset{}{C}}-CH_2-\overset{}{\underset{}{C}}\sim \\
\quad CO_2CH_3 \quad CO_2CH_3
\end{array}
\quad (10)
$$

The appearance of large amounts of low polymer in the volatiles and the rapid drop in molecular weight of the soluble portion of the polymeric residue indicate the frequent occurrence of transfer reactions and the existence of radicals of type (G) is fairly certain. The crosslinking reaction competes with chain scission and, if it occurs frequently enough, can lead to the formation of an infinite network.

Examination of a range of poly(methyl acrylate) samples indicated that gel formation is dependent on two main factors in the preparative history of the sample—the temperature of polymerization and the degree of conversion of monomer to polymer. The effect of polymerization temperature on gel formation is shown in figure 2 in which the most notable feature is the minimum at $\sim$50 °C. At 238 °C virtually no volatiles are evolved. Measurements of the second virial coefficients of poly(methyl acrylate) samples prepared at different temperatures (fig. 3) show that the degree of branching also goes through a minimum in the region of 50 °C. The reason for this behaviour is obscure at present. Although correspondence between figures 2 and 3 is not exact the appearance of minima in each suggests that highly branched samples of this polymer have the strongest tendency to form gel during pyrolysis. As the temperature of polymerization is lowered the polymer has a higher molecular weight which would tend to push up the gel-forming tendency of the sample prepared at 40 °C. The correlation between gel formation and branch density is reinforced by the observation that the higher the conversion on polymerization, the higher the gel content on degradation. Branching in this polymer is an unavoidable consequence of free radical polymerization. It would be interesting to confirm the above view by degrading a truly linear sample of poly(methyl acrylate), possibly prepared by anionic polymerization.

In general the effects of chain branches on thermal stability are not as clearcut as those of unsaturation. There is some doubt, for example, as to the possible destabilizing role of branch points on PVC dehydrochlorination [17].
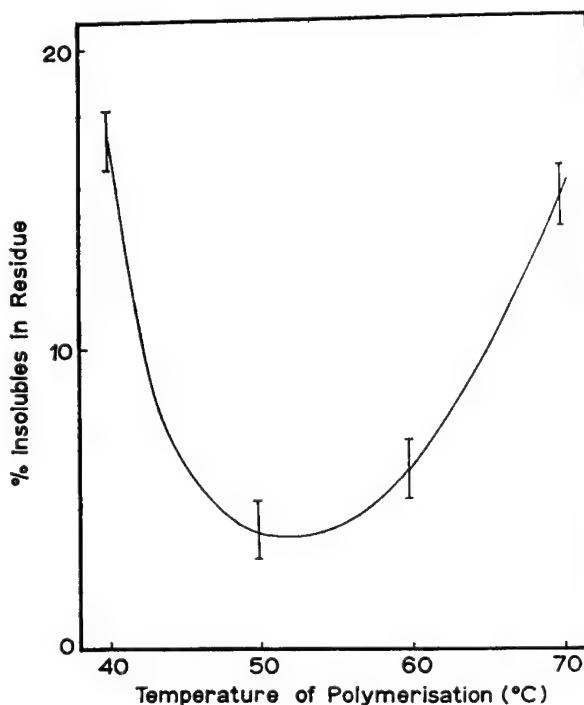

FIGURE 2. *Percent insoluble gel after 1 hr at 238° as a function of polymerization temperature.*
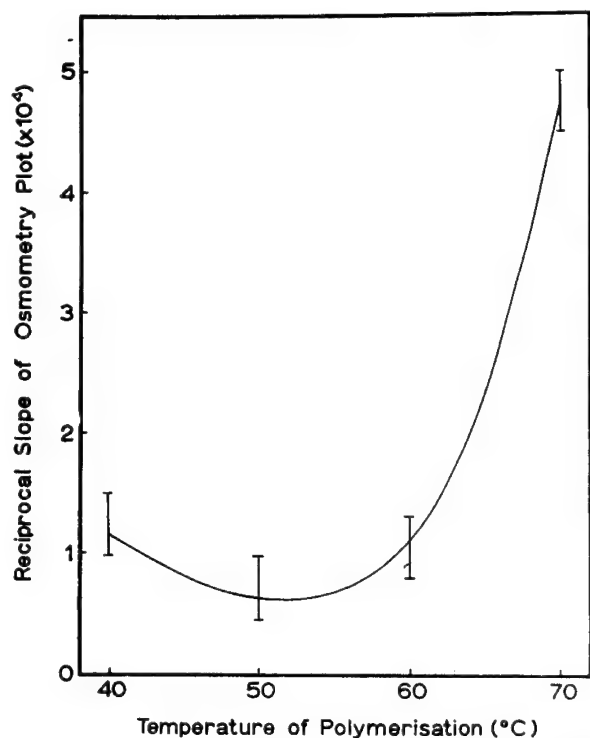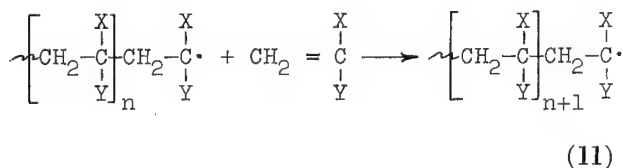
FIGURE 3. *Reciprocal osmotic slopes of poly(methyl acrylate) samples as a function of polymerization temperature.*

2.3. Head-to-head Links

It is generally accepted that addition polymerization occurs predominantly in the head-to-tail fashion.


(11)

This mode of addition is strongly favoured on steric and energetic grounds. Nevertheless the possibility of an occasional head-to-head addition can never be completely discounted. The resulting structure
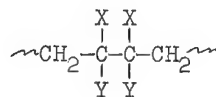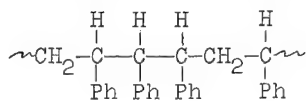

would be expected to be more thermolabile than normal backbone bonds and could provide a weak point in the chain.

The role of such linkages in the pyrolytic decomposition of polystyrene has received considerable attention against the background of a lively controversy on the question of "weak links" in this polymer [18]. Since termination of the free radical polymerization of styrene is by combination (see eq 7) each chain in the sample will contain at least one such abnormality [19]. (The additional concentration of such groups due to head-to-head addition during propagation is likely to be very small.) The proportion of head-to-head units can be substantially reduced if polymerization is conducted in the presence of an active transfer agent or if the polymerization temperature is increased to about 100 °C when disproportionation occurs. Despite their probable low concentration head-to-head units undoubtedly weaken the polymer chain. This has been proved by two independent studies. In the first of these, polystyrenes containing controlled amounts of head-to-head structures were prepared by coupling "living" polystyrene anions with iodine [20].

(12)
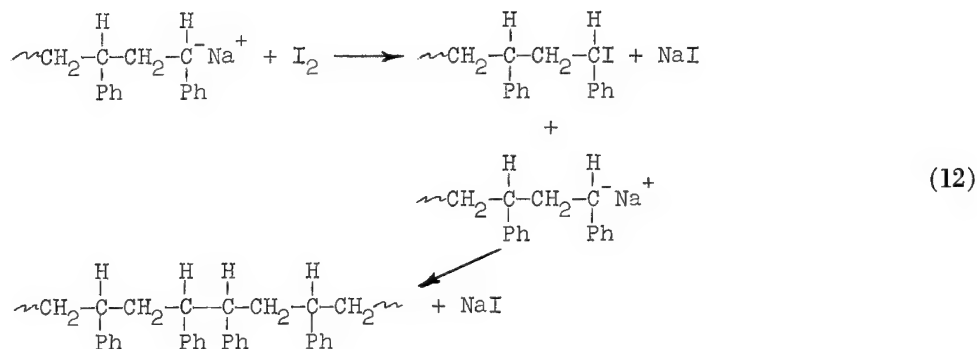
The resulting polymers were found to be more thermolabile than control samples also polymerized anionically but "killed" with methanol. In the second study [10] head-to-head structures were introduced by incorporating small amounts of stilbene during free radical polymerizations. A copolymerized stilbene unit produces the structure

$$\text{--}CH_2\text{--}\underset{Ph}{\overset{H}{\underset{|}{\overset{|}{C}}}}\text{--}\underset{Ph}{\overset{H}{\underset{|}{\overset{|}{C}}}}\text{--}\underset{Ph}{\overset{H}{\underset{|}{\overset{|}{C}}}}\text{--}CH_2\text{--}\underset{Ph}{\overset{H}{\underset{|}{\overset{|}{C}}}}\text{--}$$

which, if anything, should be slightly weaker than a head-to-head unit. Rates of bond scission at sub-volatilization temperatures for a series of such copolymers with different stilbene contents were compared with a control homopolystyrene. The results are shown in figure 4. At 280 °C the control homopolymer does not undergo appreciable chain scission. The copolymers, however, decompose rapidly at this temperature and the rate of bond scission increases with stilbene content.

An interesting preliminary study has been made of the comparative thermal stabilities of head-to-head and conventional poly(vinyl chloride) [21]. The former was prepared by chlorination of 1,4-trans-polybutadiene and therefore all the vinyl chloride units in the chain were linked head-to-head. Using
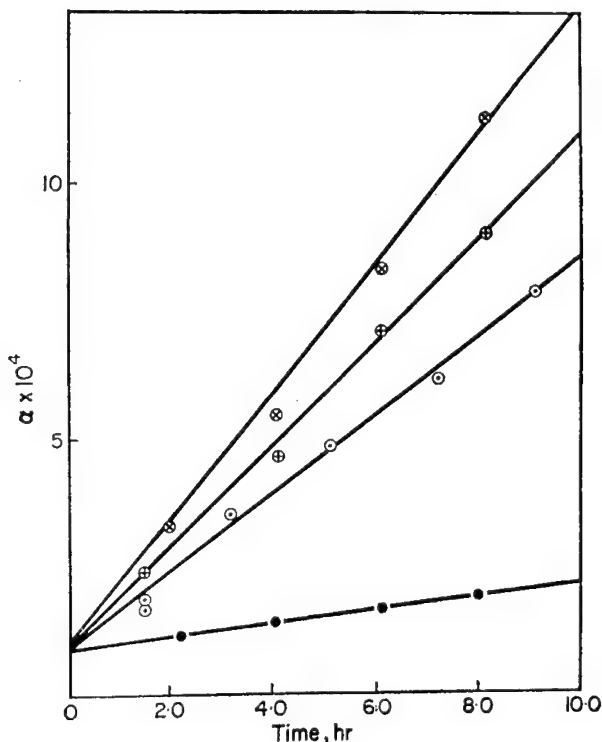
FIGURE 4. *Degree of degradation,* α, *versus time of heating for styrene homopolymer* (287°) *and styrene-stilbene copolymers* (280°).

● Styrene homopolymer.
⊙ 157, ⊕ 116, ⊗ 72, Styrene-stilbene molar ratios in copolymers.

thermogravimetric analysis it was shown that the head-to-head polymer began to lose HCl at an appreciably lower temperature than the conventional one, although at a lower rate. It follows that any head-to-head units in normal PVC could act as initiation sites for dehydrochlorination. By way of contrast, head-to-head poly(vinylidene chloride) (prepared by chlorination of polydichlorobutadiene [21] is more stable than its head-to-tail counterpart. It was suggested that this improved stability in the head-to-head polymer was due to the smaller number of hydrogen atoms adjacent to each chlorine atom and to the freedom from stripping of HCl from sequences of monomer units.

2.4. Oxidation Products

The oxidative degradation of polymers is treated in detail in other contributions to this symposium. In this section a few examples will be discussed to illustrate the effects of oxygen-containing groups in subsequent thermal degradation. Many polymers are subject to slow oxidative degradation at ambient temperatures, particularly if exposed to ultraviolet radiation.

It is widely accepted that hydroperoxides play a vital role in the early stages of oxidation of saturated materials. Numerous secondary products accumulate with the decomposition of hydroperoxide. The hydroperoxide and the secondary products may be regarded as abnormalities in the polymer chains and may initiate thermal decomposition in a number of ways. Homolytic decomposition of hydroperoxide gives rise to hydroxyl and alkoxyl radicals which can cause chain scission reactions at abnormally low temperatures, or accelerate decomposition at higher temperatures. In the case of polyethylene, it has been suggested that the combination of oxygenated structures and chain branches is largely responsible for its relative instability [22]. These oxygenated abnormalities may be introduced by incorporation of impurities during preparation or by subsequent oxidation. The degradation of polypropylene is also influenced by oxidation products. Some investigators have suggested that these include hydroperoxides [23] presumably formed by oxidation at the tertiary hydrogen atoms. Indeed, tertiary hydrogen atoms are among the more sensitive sites in polymers for oxidation. It is therefore not surprising that poly(methyl acrylate) is subject to oxidative ageing during storage and is considerably more thermally unstable as a result [24].

The effects of oxygenated structures on the thermal stability of polymers has not always been appreciated. According to Grassie [25] much of the published work on PVC degradation is complicated by the existence of oxidation products in the polymer samples.

Oxygen may be incorporated directly into a few polymers during free radical polymerization. For example, in polystyrene it is believed to form a peroxide link [26, 27].

$$(13)$$
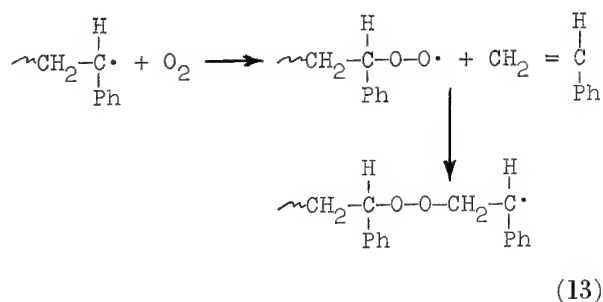
The resulting structure must be highly thermolabile and can probably form in low concentration if air is not rigorously excluded from the polymerization vessel. In figures 1 and 4 it will be noticed that the plots of α (fraction of bonds broken) versus time show a well defined ordinate intercept at zero time. This behaviour has been interpreted as resulting from a few highly reactive weak points in the polymer backbone and the possibility that these are peroxide units has been proposed [10]. This suggestion remains unproved at present but it is noteworthy that analogous data from anionically synthesized polystyrene do not show this initial rapid decomposition [11].

Because of the stringent purity conditions required and the nature of the propagating species it is improbable that oxygen would be incorporated in a similar fashion during anionic polymerization. Weir and Lawrence have attributed the increased photolytic instability of free radical polystyrenes to the same source [28].

It should be made clear that the initial precipitous drop in molecular weight of polystyrene during pyrolysis at temperatures high enough to liberate volatile material is not due entirely to the existence of weak links of any structure. This behaviour is quite characteristic of any random fragmentation process and also occurs in anionically synthesized polystyrene. The effect of any weak bonds is to accelerate this decomposition or to induce it at lower temperatures.

2.5. Other Abnormalities

Almost all of the abnormalities discussed so far reduce the pyrolytic stability of polymers. This, however, is not an invariant rule and there are one or two striking cases of abnormal structures which actually stabilize the polymer chains. An example of this concerns polymethacrylonitrile. Samples of this polymer prepared with very pure monomer can evolve nearly quantitative yields of monomer if heated rapidly to about 300 °C. This polymer is, however, sensitive to coloration reactions [29] which occur fairly rapidly around 200 °C and even lower when traces of methacrylic acid are present as comonomer. The coloration reaction is due to the formation of conjugated carbon-nitrogen double bonds.
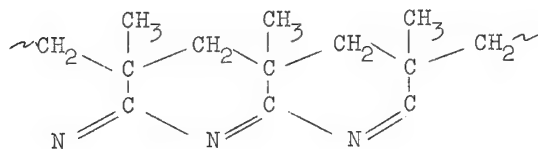
The cyclic or ladder structure produced blocks the unzipping reaction which is the source of monomer. Similarly, the formation of anhydride structures in higher polymethacrylates (as a consequence of olefin elimination) blocks the unzipping process which produces monomer [30].

3. Conclusions

The examples discussed above illustrate some of the effects of abnormalities on the degradation mechanism. In many cases, though not all, the effect is on the initiation step of the degradation but because of the susceptibility of polymers to radical chain reactions (e.g. unzipping of poly(methyl methacrylate)) or to neighbouring group effects (e.g. elimination of acetic acid from poly(vinyl acetate)) the abnormality can effectively lower the thermal stability of a large proportion of the sample.

It is also noticeable that much of the evidence for the existence of labile abnormalities is indirect. This is particularly true of polystyrene. The anionically synthesized polymer is considerably more stable than free radical material and it is a reasonable conclusion that thermolabile structures exist in the latter, but it has not been possible to follow the concentration of these with time of pyrolysis. Indeed, there has been no *direct* identification of thermolabile irregularities in this polymer. This point underlines one of the practical difficulties in pyrolysis studies of polymers, namely, the sensitivity of the polymer to concentrations of abnormal structures which are often too low to be detected by conventional means. Nevertheless, for meaningful kinetic and mechanistic studies the starting material must be as fully characterized as possible, and it is the responsibility of the investigator to consider irregularities in this context.

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Discussion

M. J. Brock (The Firestone Tire and Rubber Company):

I was greatly interested in the comments of Gordon Cameron with respect to thermolabile irregularities which can be incorporated into the polymer structure during polymerization and how they can affect degradation reactions. We have recently observed that the microstructure of polyisoprene polymers has a great affect upon some of the products obtained during pyrolysis.

The polyisoprene system is convenient for study since a wide variety of microstructures can be prepared as shown below by varying the catalyst system.
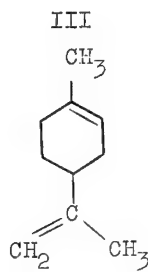
	Percent cis 1,4 units	Percent trans 1,4 units	Percent 1,2 units	Percent 3,4 units
Natural Rubber (cis PI)	97.6	0	0	2.4
trans PI	0	98.0	0	2.0
Ziegler PI	96.8	0	0	3.2
Lithium PI	93.8	0	0	6.2
Alfin PI	10.9	59.2	5.1	24.9
Emulsion PI	24.4	62.0	6.1	7.5
Sodium PI	0.0	44.0	6.0	50.0
Li, PI, ether system	11.7	25.0	5.2	58.0

Everyone is familiar with Dr. Wall's work on the pyrolysis of natural rubber, cis polyisoprene, to produce the monomer, isoprene, by an unzipping mechanism. If the unzipping reaction involves two isoprene units at a time, then dimers could be produced also during thermal degradation. There are four possible alkyl substituted cyclohexene dimers of isoprene.

All of these dimers are found in varying degrees in the pyrolysis products of polyisoprenes having different microstructures. Examination of the data obtained indicates that cis and trans 1,4 polymers produce mostly dimer III and some dimer II. Polymers containing 1,2 and 3,4 vinyl structures produce increasing amounts of dimer II depending upon the vinyl content. Extremely high vinyl polymers produce mostly dimers III and IV. Dimer I was produced in significant quantities only from Alfin, emulsion, and sodium polyisoprenes. Assuming a two isoprene unit "backbiting" mechanism, dimer I can only be produced from head-head structures in polyisoprene.

I
1,4-Dimethyl-4-vinylcyclo-hexene-1
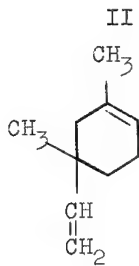
II
1,5-Dimethyl-5-vinylcyclo-hexene-1

III
Dipentene

IV
Diprene

Microozonolysis data have been obtained on these samples and only Alfin, emulsion and sodium polyisoprenes give substantial quantities of 2,5 hexanedione to indicate the presence of head-head isoprene units in these polyisoprene polymers.

These results are further evidence that pyrolysis products and probably pyrolysis kinetics are affected by irregularities incorporated into the polymer structure during polymerization. I would like to reemphasize the statements of Gordon Cameron. Complete characterization of polymer composition and structure is extremely important where kinetic and mechanistic studies are being contemplated.

G. G. Cameron:

Dr. Brock's contribution is a very elegant illustration of how the fine structure of a polymer can affect the products of degradation. It also underlines the importance of considering the preparative history of each sample before making any generalizations.

S. E. Wentworth (Army Materials and Mechanics Research Center):

Dr. Cameron, during your talk you mentioned the importance of oxidation in the thermal degradation of polymers. You further mentioned that tertiary protons on the polymer backbone were most susceptible to attack by oxygen. I am aware of at least one study on polyacrylonitrile where it is stated that secondary protons are attacked in preference to tertiary. Would you comment on this?

The study cited in the question is by J. Brandrup and L. H. Peebles, Jr., Macromolecules 1, 64 (1968).

G. G. Cameron:

In hydrocarbon polymers tertiary protons are most susceptible to attack by oxygen. When strongly electron withdrawing groups are attached to the tertiary carbon atom, however, oxygen attack on the proton is diminished. Under these conditions oxidative attack may occur at secondary protons. This point is discussed in detail by Brandrup and Peebles [Macromolecules 1, 66–69 (1968)].

J. H. Magill (University of Pittsburgh):

In earlier papers of the sessions, notably those of L. Wall and G. G. Cameron, much attention was given to question of polymer molecular weight but it was Dr. Brock of Firestone (a speaker from the floor) who pointed out that the polymer microstructure was very important. He illustrated his remarks with polyisoprenes. In this connection, I wish to inquire if either L. Wall or G. G. Cameron have compared the relative decomposition rates of isotactic with atactic well-characterized polymer systems (e.g. polystyrenes). It seems at first sight that the kinetics would be affected by the polymer tacticity.

G. G. Cameron:

I am not aware that "much attention was given to polymer molecular weight" in my paper. I have not carried out studies of the effects of tacticity on polymer degradation but from the limited data in the literature it seems that changes in tacticity do not have a significant effect on the mechanism of decomposition of polymers in categories (a) and (b). Some differences in energies of activation or kinetic coefficients are to be expected, however. For example it has been shown that for poly(methyl methacrylate) the kinetic chain lengths of the unzipping reaction are greater in the atactic and syndiotactic polymers than in the isotactic polymer. (Jellinek in The Stereochemistry of Macromolecules, Vol. 3, Ed. A. D. Kettley, Dekker, N.Y. 1968, pp. 378–385). In studying effects of tacticity on the detailed kinetics of degradation care must be taken to ensure that the effects of tacticity are not obscured by the presence or absence of abnormal structures in the polymer samples prepared by different synthetic methods.

L. A. Wall (National Bureau of Standards):

The tacticity of a polymer chain would be expected to have only small effects on the kinetics of thermal decomposition, assuming that one would be comparing the decompositions of both the atactic and tactic polymers in the melt. The differences in the energies of formation between the various tactic structures are only a few hundred small calories. Thus, large kinetic effects, for instance on the thermal stability, are not anticipated. A good discussion of the current literature on this point can be found in the article mentioned above: Degradation of Stereoregular Polymers, by H. H. G. Jellinek (Chapter 10, The Stereochemistry of Macromolecules, Vol. 3, editor Ketley, publisher Dekker).

F. H. Winslow (Bell Telephone Laboratories):

In the first section of Dr. Cameron's paper, the relatively high monomer yield from polystyrene pyrolysis was attributed to the low transfer rate of the polystyryl radical. It was inferred that α-hydrogen atoms were readily available for reaction. Most likely the phenyl ring does have a stabilizing effect on the propagating radical but the enormous stabilizing effect it has on the α-hydrogens may be much more important as your work has so clearly shown. For example, cumene and the isopropyl groups in poly(p-isopropylstyrene) oxidize readily in the dark at 80 °C. But the α-hydrogens in polystyrene are remarkably resistant to oxidation at 140 °C. If the α-hydrogens on the polymer chain were typical allylic hydrogens readily accessible to molecular oxygen or other oxidation intermediates, the oxidation rate of the polymer would be similar to that of cumene or at least to that of poly(p-isopropylstyrene).

G. G. Cameron:

I agree with Dr. Winslow that steric effects must also play some part in the degradation mechanism. This is an important point and I am glad that Dr. Winslow has raised it. This does not detract from my own observation, however, that the reactivity of the abstracting radical has to be considered along with other factors.

# On Certain Problems Connected With the Inhibited Oxidation Theory

Yu. A. Shlyapnikov

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow

The oxidative reactions of organic compounds and polymers are discussed in terms of free radical mechanisms, with particular emphasis on initiation, inhibition, and stabilization phenomena.

Key words: Antioxidants; inhibition of oxidation; initiation of oxidation; oxidation mechanism; oxidation theory.

The main reason for aging of organic compounds is their interaction with air oxygen. The oxidation of hydrocarbons is that investigated most extensively. It occurs also with compounds containing molecular hydrocarbon fragments. The mechanism of hydrocarbon oxidation had been essentially elucidated by 1946. It was found to involve two alternating steps of chain propagation [1, 2][1]

$$R \cdot + O_2 \rightarrow RO_2 \qquad (1)$$

$$RO_2 + RH \rightarrow ROOH + R \cdot \qquad (2)$$
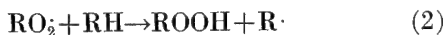
Here RH is the hydrocarbon and R· the relevant free radical.

Nevertheless the mechanism of hydrocarbon oxidation cannot be considered as completely established.

The sources of free radicals initiating oxidation usually represent certain additives, various types of radiation including light, and mechanical degradation. In the case of "noninhibited" oxidation the main sources of free radicals are suggested to be the reactions involving various impurities. The author has no knowledge of papers on measurements of the rates of direct interaction between hydrocarbons and molecular oxygen. Such interaction is considered to be the initiating step:

$$RH + O_2 \rightarrow R \cdot + HO_2 \qquad (3)$$

When hydroperoxide is formed in the course of oxidation, its decomposition becomes the main source of free radicals. Without discussing yet the mechanism of this reaction in detail, let us write it in the form
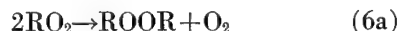
$$ROOH \xrightarrow{(RH...)} \delta R \cdot + \text{inactive products} \qquad (4)$$

Chain termination may occur by recombination of two radicals, for example

$$R \cdot + R \cdot \rightarrow R_2 \text{ (hydrocarbon)} \qquad (5)$$

$$RO_2 + RO_2 \rightarrow \text{inactive products}$$
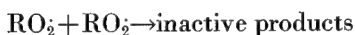
Recombination reactions yielding peroxide, such as

$$RO_2 + R \cdot \rightarrow ROOR \qquad (6)$$

or

$$2RO_2 \rightarrow ROOR + O_2 \qquad (6a)$$

terminate the chain only when further peroxide decomposition yields on an average less than two free radicals per peroxide group.

The hydroperoxide group decomposition should be discussed in detail.

Decomposition of a hydroperoxide group to two radicals

$$ROOH \rightarrow RO \cdot + \cdot OH \qquad (7)$$

requires a high activation energy. In the solid or liquid phase this reaction will be negligible because of the cage effect that considerably decreases the rate of reaction (7). Another reason is the competition of more fast reactions, such as [3, 4]

$$
ROOH + RH
\begin{cases}
\nearrow RO \cdot + R \cdot + H_2O \\
\searrow ROH + R \cdot + OH \cdot
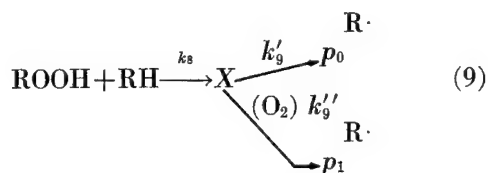\end{cases}
\qquad (8)
$$
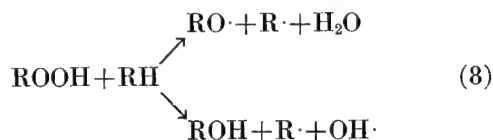
Intracage interaction of radicals occurring by reaction (8) would not affect the reaction rate, but would only decrease the average number of radicals emerging from the cage.

When foreign molecules, such as O_2, are present in the cage, the probability of emergence of a free radical becomes higher, as recombination of the resulting radical RO_2 with RO· or OH, as well as that of interaction between RO_2 and the surrounding RH, would differ from the rates of similar R· reactions.

Let us denote by X the cage containing the radical pair. Then the scheme of chain branching will be

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[1] Figures in brackets indicate the literature references at the end of this paper.

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$$ROOH+RH \xrightarrow{k_8} X \begin{array}{c} \overset{k_9'}{\nearrow} p_0 \\ R\cdot \\ \searrow (O_2)\ k_9'' \\ R\cdot \\ \searrow p_1 \end{array} \qquad (9)$$

where p_0 and p_1 are the probabilities of the emergence of one radical out of a cage containing no (p_0) and containing O_2.

In accordance with (9)

$$\delta = \frac{[p_0 k_9' + p_1 k_9''[O_2]]X}{k_8[ROOH][RH]} = \frac{p_0 k_9' + p_1 k_9''[O_2]}{k_9' + k_9''[O_2]} \quad (10)$$

or for low concentrations of O_2, for which $k_9' \gg k_9''[O_2]$

$$\delta = p_0 + p_1 \frac{k_9''}{k_9'}[O_2] = \delta_0 + \delta_1[O_2] \qquad (10a)$$

The relation (10a) was confirmed experimentally when studying the degradation of hydroperoxide groups of polypropylene in O_2. Use was made of radicals of a definite type R_j, such as $CH_3^\cdot$ or microradicals with end free valence, capable of depolymerization by scheme

$$-CH_2-CH(CH_3)CH_2^\cdot \rightarrow CH_2^\cdot + CH_3-CH=CH_2$$
$$(11)$$
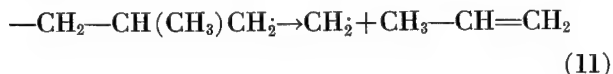
Both radicals can also react with the surrounding species RH (with a constant k_{1j}) and with $O_2(k_{2j})$. The resulting R_j concentration would be

$$[R_j] = \frac{\delta_j k_8[RH][ROOH]}{k_{1j}[RH] + k_{2j}[O_2]} \qquad (12)$$

and at $\delta_j = $ const would tend to zero with increasing $[O_2]$ pressure. Since the concentration of R_j radicals tends to a certain limit, δ_j depends on $[O_2]$ according to (10a). The methane and propylene yields obtained by first-order R_j conversions tend to limits differing from zero with increasing $[O_2]$ (fig. 1, curves 1 and 2).
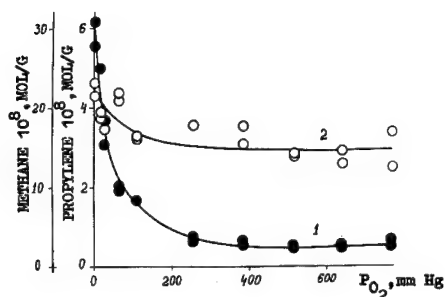
FIGURE 1. *Yields of methane (a) and propylene (2) in polypropylene hydroperoxide decomposition as a function of oxygen pressure.*

100 °C, time of decomposition 60 min, [ROOH] = 3.6.100⁴ mol/g.

Until recently the dependence of degenerate chain branching probability δ on O_2 pressure was usually neglected.

Most investigations on the mechanism of hydrocarbon oxidation were carried out at temperatures up to 150°. One of our papers deals with oxidation of linear polyethylene at temperatures higher than 200°. At high temperatures (200–400 °C) the kinetics of oxidation becomes different. Within this temperature range the oxidation rate dependence on oxygen pressure becomes first order in $[O_2]$ (fig. 2). The effective activation energy decreases from 20–30 to 1–2 kcal/mol and a decrease in oxidation rate with increasing temperature is observed in some cases (fig. 3). Obviously, the value δ increasing with temperature mainly due to the rapid increase in δ_0 reaches its stoichiometric limit and depends no **more on oxygen pressure.**
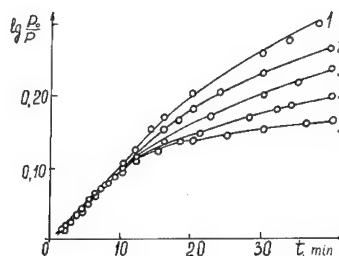
FIGURE 2. *Curves for oxygen absorption in polyethylene oxidation at 360 °C plotted as $\log p_0/p$ versus time.*

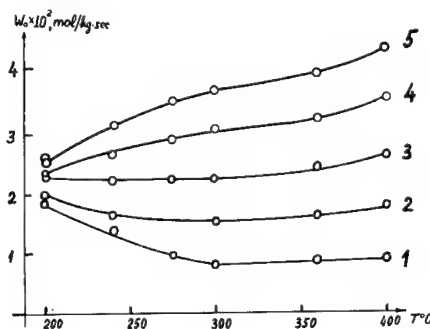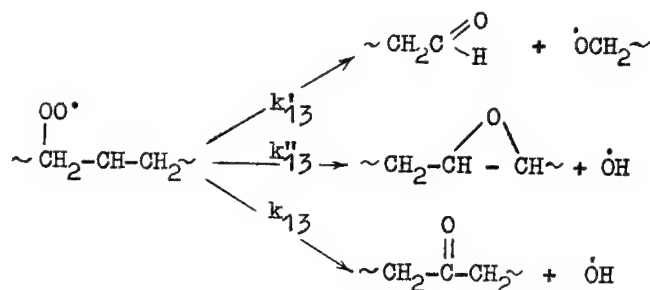Oxygen pressure 20 mm (1); 40 mm (2); 60 mm (3); 80 mm (4) and 100 mm (5).

FIGURE 3. *Initial rate of polyethylene oxidation as a function of temperature.*

Oxygen pressure 20 mm (1); 40 mm (2); 60 mm (3); 80 mm (4) and 100 mm (5).

At the same time $RO_2^\cdot$ decomposition at a rate increasing with temperature (E_{eff} 20 kcal/mol) becomes the main route of $RO_2^\cdot$ conversions. The decomposition of $RO_2^\cdot$ in polyethylene yields, in particular, OH radicals and epoxy-groups that can be detected by ir-spectroscopy

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$$\sim CH_2-CH-CH_2\sim \quad \xrightarrow{\substack{k'_{13} \\ k''_{13} \\ k_{13}}}$$

with $OO^\cdot$ on the central carbon, branching to:

$$\sim CH_2C\overset{\nearrow O}{\underset{\searrow H}{}} \quad + \quad {}^\cdot OCH_2\sim$$

$$\sim CH_2-CH\overset{O}{\underset{}{-}}CH\sim + {}^\cdot OH$$

$$\sim CH_2-\overset{O}{\overset{\|}{C}}-CH_2\sim + {}^\cdot OH$$

(13)

The main route of chain termination is now the recombination of most mobile radicals OH with radicals R· of various types:

$$R\cdot + \dot{O}H \rightarrow ROH \tag{14}$$

$$RH + \dot{O}H \rightarrow R\cdot + H_2O \tag{15}$$

Taking into account reaction (15) and assuming that $k_{14}[R\cdot] \ll k_{15}[RH]$, the rate of high-temperature oxidation will be

$$W = k_1[R\cdot][O_2] = \frac{\delta k_1 k_2 k_{15}[RH]^2}{2(k''_{13}+k'''_{13})k_{14}} \tag{16}$$

New facts were observed in investigating the oxidation of a solid crystalline hydrocarbon polymer (polypropylene). Its total crystallinity depends on its chain regularity and does not depend on the technique of sample preparation. Nevertheless, the induction period of oxidation for samples prepared by rapid cooling of the melt and consisting of small spherules is far shorter than that for samples consisting of big spherules and prepared by slow cooling.

In both cases oxidation occurs in amorphous regions consisting mainly of interspherulic substance for rapidly cooled samples, and of itraspherulic, interfebrilic substance for slowly cooled samples. One of the probable explanations would be the difference in thickness of layers of amorphous regions. According to Semenov, the rate of chain termination on the reactor wall [5] is

$$W_g = ad^{-2} \tag{17}$$

Consequently, the length of unbranched oxidation chains will be

$$\nu = 1 + \frac{k_2[RH]}{W_g} = 1 + k_2[RH]d^2a^{-1} \tag{18}$$

and the factor of autoacceleration (coefficient in equation $W = W_0 \exp \zeta\tau$) is

$$\varphi = \left(\frac{\nu\delta - 1}{\theta}\right)$$

$$= k_8[RH]\left\{\frac{(1+k_2[RH]d^2a^{-1})(p_0 k'_9 + p_1 k''_9[O_2])}{k'_9 + k''_9[O_2]} - 1\right\} \tag{19}$$

where θ is the average lifetime of a chain branching product, i.e., $1/k_8[RH]$.

The induction period τ is determined from $W = W_0 \exp\varphi\tau = \text{const}$, i.e., $\varphi\tau = \text{const}$. Hence

$$\tau = \frac{\text{const}}{\varphi} = \frac{\text{const}}{k_8[RH]}$$

$$\times \frac{k'_9 + k''_9[O_2]}{\substack{k'_9(p_0 k_2[RH]d^2a^{-1}+p_0-1) \\ + k''_9(p_1 k_2[RH]d^2a^{-1}+p_1-1)[O_2]}} \tag{20}$$

When the oxygen pressure is high enough, expression (19) can be written as

$$\tau = \frac{A}{[O_2]} + B = \frac{A'}{p} + B \tag{21}$$

where p is the oxygen pressure.

It will be seen from figure 4 that the function of type (20) is actually fulfilled, the coefficients A' and B depending on conditions of sample preparation.

At high degrees of oxidation recombination of free radicals becomes the main route of chain termination and the rates of oxygen consumption appear to be almost identical for different samples.

Inhibitor [IH] added to the oxidizing substance terminates the kinetic chains, mainly by reaction with peroxide radicals $RO_2^\cdot$, e.g., [6]
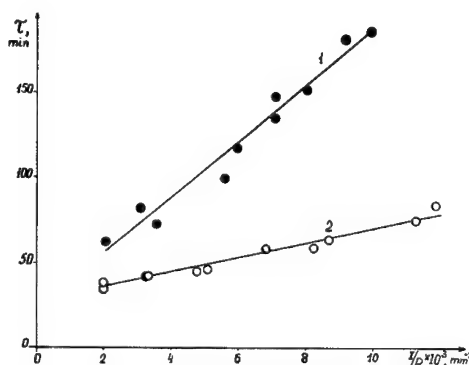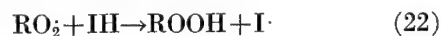
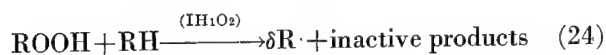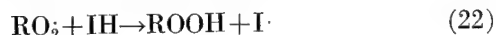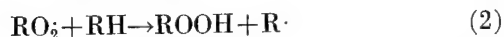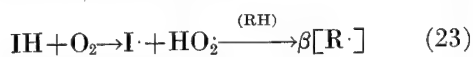$$RO_2^\cdot + IH \rightarrow ROOH + I\cdot \tag{22}$$

FIGURE 4. *Induction period for polypropylene oxidation as a function of the oxygen pressure reciprocal (130°).*

1—slowly cooled samples; 2—rapidly cooled samples.

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The inactive radicals I· yielded by this reaction mostly disappear and do not initiate new chains. But the actual inhibitor function is not confined to chain termination. Phenols and amines used as inhibitors are more readily oxidized than the main substance, and initiate oxidation of the latter [7]. This process reduces the inhibitor efficiency. But to our opinion for more important is the participation of the inhibitor in degenerate chain branching. It was stated above that most radicals formed from the hydroperoxide group recombine in the cage. For instance, the yield of light-weight methyl radicals formed by decomposition of solid polypropylene hydroperoxide at $100°$ is $\delta = 7 \times 10^{-3}$, and its value in the melt must be much lower. A particle penetrating into the cage and destroying one of the free radicals in a pair will prevent destruction of the second radical and the emergence of free radicals out of a cage containing such particles will approach unity. Common inhibitors containing one active group, though capable of destroying consecutively both radicals of the pair, will react with the first and second radicals at different rates. That must also enhance the radical emergence. It may be considered approximately that the cage volume is $(10\ A)^3 = 10^{-24}$ l. When the inhibitor increases the probability of radical emergence to 0.5, only 0.2 percent of the inhibitor content in cages is sufficient for increasing δ from 1×10^{-3} to 2×10^{-3}. The inhibitor concentration will then be $10^{24} \times 2 \times 10^{-3} = 2 \times 10^{21}$ molecules/litre $= 3.3 \times 10^{-3}$ mol/litre. The common concentrations of inhibitors are $(5-30) \times 10^{-3}$ mol/litre. That is sufficient for a great change of δ.

The inhibitor effect on the probability of degenerate chain branching was proved directly by Pudov's investigations [8] on polypropylene hydroperoxide decomposition in the presence of ionol.

Taking the above into account, the scheme of oxidation in the presence of an inhibitor [IH] will be:

$$RH + O_2 \rightarrow R\cdot + HO_2^{\cdot} \tag{0}$$

$$IH + O_2 \rightarrow I\cdot + HO_2^{\cdot} \xrightarrow{\text{(RH)}} \beta[R\cdot] \tag{23}$$

$$R\cdot + O_2 \rightarrow RO_2^{\cdot} \tag{1}$$

$$RO_2^{\cdot} + RH \rightarrow ROOH + R\cdot \tag{2}$$

$$RO_2^{\cdot} + IH \rightarrow ROOH + I\cdot \tag{22}$$

$$ROOH + RH \xrightarrow{\text{(IH\textsubscript{1}O\textsubscript{2})}} \delta R\cdot + \text{inactive products} \tag{24}$$

When a hydroperoxide reducing agent [Y], for example dialkyl sulfide [9], is added to the system along with the inhibitor [IH], another step must be added to the scheme

$$ROOH + Y \rightarrow \text{inactive products} \tag{25}$$
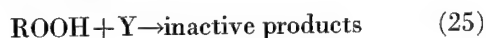
This scheme does not take into account the termination by recombination, as its rate is negligibly low in the presence of an inhibitor.

The dependence of degenerate chain branching probability on the inhibitor concentration may be given with sufficient accuracy by an expression similar to (10a)

$$\delta = \delta_0 + \delta_i[IH] \tag{26}$$

Allowance for the dependence of δ on [IH] permits explaining virtually all phenomena observed in studying inhibited oxidation of hydrocarbons and polyolefins. Among them of greatest interest are the critical concentrations. The set of balance equations for R·, $RO_2^{\cdot}$ and hydroperoxide will be:

$$\frac{d[R\cdot]}{dt} = \alpha k_0[RH][O_2] + \beta k_{23}[IH][O_2]$$
$$+ k_1[R\cdot][O_2] + k_2[RO_2^{\cdot}][RH] + \delta k_{24}[ROOH][RH] \tag{27}$$

$$\frac{d[RO_2^{\cdot}]}{dt} = k_1[R\cdot][O_2] - k_2[RO_2^{\cdot}][RH]$$
$$- k_{22}[RO_2^{\cdot}][IH] \tag{28}$$

$$\frac{d[ROOH]}{dt} = k_2[RO_2^{\cdot}][RH] + k_{22}[RO_2^{\cdot}][IH]$$
$$- k_{24}[ROOH][IH] - k_{25}[ROOH][R_2\delta] \tag{29}$$

Using the Bodenstein-Semenov method [10], i.e. assuming that $d[R\cdot]/dt = 0$: $d[RO\cdot]/dt = 0\cdot$, but $d[ROOH]/dt \neq 0$, we can find the solution:

$$[ROOH] = Ae^{\varphi t} + B \tag{30}$$

where, assuming $[R_2S\cdot] = 0$

$$\varphi = \varphi_0 = \frac{k_{24}[RH]}{k_{22}[IH]}\{\delta_i k_{22}[IH]^2$$
$$+ (\delta_i k_2[RH] - k_{22} + \delta_0 k_{22})[IH] + \delta_0 k_2[RH]\} \tag{31}$$

and when $[R_2S\cdot] \neq 0$

$$\varphi = \frac{k_{24}[RH]}{k_{22}[IH]}\{\delta_i k_{22}[IH]^2$$
$$+ (\delta_i k_2[RH] - k_{22} + \delta_0 k_{22})[IH] + \delta_0 k_2[RH]\}$$
$$- k_{25}[R_2S] = \varphi_0 - k_{25}[R_2S] \tag{32}$$

The kinetics of oxidation depends on the sign of ζ. When $\varphi > 0$, the hydroperoxide concentration will rise autocatalytically. When $\varphi < 0$, the hydroperoxide concentration will be an unambiguous function of the rate constants and concentrations of RH, O_2 and IH.

Solution of equation $\varphi([IH]) = 0$ gives the critical values of inhibitor concentration

$$[IH]_{cr} = \frac{(1-\delta_0)k_{22} - \delta_i k_2[RH]}{2_i k_{22}}$$

$$\pm \frac{\sqrt{\delta_i^2 k_2^2[RH]^2 - 2(1-\delta_0)\delta_i k_2 k_{22}[RH] + (1-\delta_0)^2 k_{22}^2}}{2_i k_{22}} \tag{33}$$

When $\delta_i k_2[\mathrm{RH}] - (1 - \sqrt{\delta_0})^2 k_{21} > 0$, equation $\varphi([\mathrm{IH}]) = 0$ has no real solution. In this case $\varphi > 0$, independently of the inhibitor concentration, i.e. the process is not stationary at any inhibitor concentration. If $\delta_i k_2[\mathrm{RH}] - (1 - \sqrt{\delta_0})^2 k_{21} < 0$, the second-order equation $\varphi([\mathrm{IH}]) = 0$ (see 31) can have two real solutions namely $[\mathrm{IH}]$ and $[\mathrm{IH}]_2$, which we call lower and upper critical concentrations. When $[\mathrm{IH}] < [\mathrm{IH}]_1$, $\varphi > 0$ and, in accordance with (30), the oxidation process is autocatalytic. If $[\mathrm{IH}] = [\mathrm{IH}]_1$, becomes zero and remains negative up to $[\mathrm{IH}] = [\mathrm{IH}]_2$. Within this range oxidation is stationary. When $[\mathrm{IH}] > [\mathrm{IH}]_2$, oxidation again becomes autoaccelerated and its mean rate simply increases. The strong bends of curves for the induction period as a function of the inhibitor concentration correspond to critical concentrations $[\mathrm{IH}]$ and $[\mathrm{IH}_2]$ (fig. 5).

In the case of weak antioxidants, i.e. when $\varphi[\mathrm{IH}] > 0$ at any $[\mathrm{IH}]$, oxidation can be made stationary by addition of a substance $\mathrm{R}_2\mathrm{S}$ reducing hydroperoxide. At a sufficient concentration of $\mathrm{R}_2\mathrm{S}$ equation $\varphi = \varphi_0 - k_{24}[\mathrm{R}_2\mathrm{S}] = 0$ will also have two positive solutions. Such a conversion of a weak antioxidant into a strong one by action of substances reducing hydroperoxides is well known as synergism. The low critical concentration $[\mathrm{IH}]_1$ of the weak antioxidant in the presence of didecyl sulfide is illustrated in figure 6. The effective antioxidant hinders oxidation converting the autocatalytic
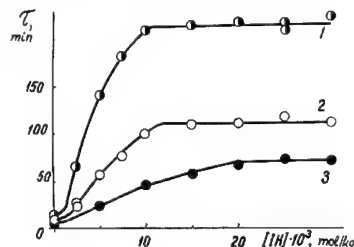
FIGURE 5. *Induction period for polypropylene oxidation as a function of the 2,2'-methylene-bis(4-chloro-6-tert-butylphenol) concentration.*

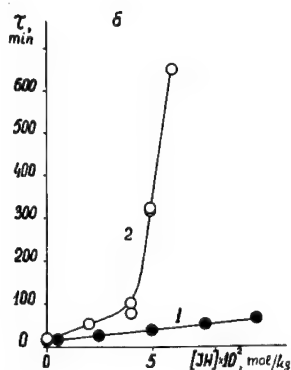180° (1); 190° (2) and 200°C (3); P0₂ = 300 mm.

FIGURE 6. *Induction period for oxidation of pure polypropylene (1) and of propylene containing didecyl sulfide, 0.08 mol/kg, as a function of 2,4,6-triterbutylphenol (200°C).*
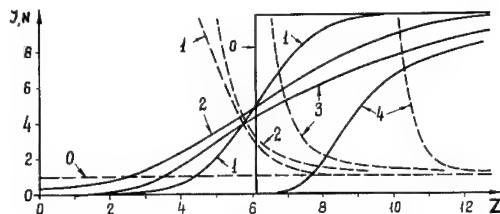
FIGURE 7. *Distribution of dimensionless concentrations of inhibitor I and active center N (dotted line) in various time intervals.*

$t = 0$ (0); 1 (1); 5 (2); 12.5 (3); and 17.5 conditional units (4). The uninhibited part size exceeds the critical value.

process into a stationary one. At the same time the common antioxidants, usually phenols and amines, that become readily oxidized, initiate oxidation. However, though the stationary reaction rate is increased by initiation, it remains many times lower than that of uninhibited oxidation. Thus, the main function of the antioxidant is the conversion of an unstationary process into a stationary one, and the theory of the antioxidant action is essentially that of critical phenomena in inhibited oxidation. In some cases the antioxidant efficiency can be predicted from its molecular structure.

The autocatalytic increase in the reaction rate can not continue infinitely. Oxidation reaches its limit due to the rapid increase in the radical recombination rate and becomes stationary. But the rate of such a stationary reaction is by many orders of magnitude higher than those of both unstationary and stationary inhibited reactions.

Some investigations have been carried out recently on the oxidation of unevenly inhibited samples. It was found [11] that if one part of the sample is deprived of the inhibitor, a fast reaction initiated in this part of the sample can propagate over the whole sample (fig. 7). The minimal size required for the uninhibited domain to become the center of fast oxidation depends on the inhibitor concentration in the remaining part of the sample. For this reason the curves for the induction period as a function of the average inhibitor concentration are markedly different for uniformly inhibited propylene and for a polymer consisting of spheric particles (0.1 mm) containing the inhibitor on their surface only (fig. 8).
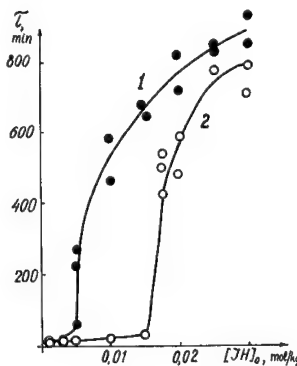
FIGURE 8. *Induction period for polypropylene oxidation as a function of $(\mathrm{CH}_3)_2\mathrm{Si}(\mathrm{OC}_6\mathrm{H}_4\mathrm{HNC}_0\mathrm{H}_5)_2$ concentration, for uniform (1) and nonuniform mixing (2) (200°C).*

The questions discussed above certainly do not cover all theoretical problems connected with practical stabilization of organic compounds.

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Discussion

F. R. Mayo (Stanford Research Institute):

While Dr. Shlyapnikov's manuscript contains some new and interesting ideas and data, some of the reactions and equations proposed deserve some comment. Reactions 8 can hardly occur in one step. I know of no adequate precedent for rearrangements of peroxy radicals by reactions 13' and 13''. The molecular products indicated probably arise via alkoxy radicals and hydroperoxide molecules, respectively. While 13'' has adequate precedent, cyclic ethers with larger rings (preferably tetrahydrofuran derivatives) are formed much more easily from *n*-alkanes. Reaction 14 violates the general principle that termination involves mostly the least reactive and most plentiful radicals; I would expect HO· radicals to disappear by 15 before they could find an alkyl radical for 14.

The set of equations on page 72 neglects at least two reactions which are probably important, termination by $RO_2^- + I^-$ and reinitiation by $I^- + RH$. Without allowance for these, the subsequent rate expressions cannot be exact although the conclusions may be qualitatively useful.

**R. E. Florin** (National Bureau of Standards):

In relating induction period to geometry of amorphous regions, the Semenov equation (17) leads to the right answer but its use can be questioned on physical grounds. Wall terminations are important in gas reactions because of the need to remove excess energy. In condensed systems a preference for wall termination is harder to understand. Might not the longer induction periods in slowly cooled polymer be associated instead with a more tortuous diffusion path for O_2 and a consequent local deficiency in the $k_q''[O_2]$ contribution?

Also, the lines 1 and 2 in figure 4 seem to have a common intercept, implying equal values of B in eq (21). In contrast, the expansion of eq (20) in powers of $\dfrac{1}{[O_2]}$ calls for a term B varying with the size parameter d^2.

In fluorination, it is easy to observe a process analogous to direct initiation, $RH + O_2 \rightarrow R^- + HO_2^-$, reaction (3) in Shlyapnikov's text. If dilute F_2 is allowed to flow over a finely divided polymer in an ESR cavity, free radical spectra appear rapidly. With polystyrene fluff and 2 percent F_2 in He intense spectra appear in a single scan time (2 min) but are largely due to peroxy radicals RO_2^- with only weak shoulders from hydrocarbon radicals. Polyethylene, 2×10^{-5} m film, with 5 percent F_2, requires 10 min to develop full intensity, but its hydrocarbon radical spectrum is better separated and more intense. Polymer radical ESR spectra have been produced previously by the action of H atoms on a fluff of polystyrene [1], $H^- + RH \rightarrow R^- + H_2$. With fluorine, the molecular form is sufficiently reactive, $F_2 + RH \rightarrow R^- + F^- + HF$. The energy liberated presumably breaks up pair correlation and delays recombination. Molecular fluorine has been used to initiate polymerization [2], and a dissociative addition has been observed already by ESR [3],

$$F_2 + CH_2{=}CH{-}CH{=}CH_2$$

$$\rightarrow FCH_2CHCH{=}CH_2 + F^-.$$
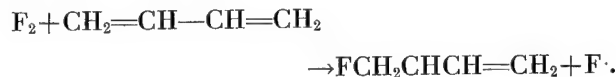
In the latter case, only peroxy radicals and no primary hydrocarbon radicals were observed. The peroxy radicals observed in these experiments arise from reaction of primary radicals with oxygen, usually present in commercial fluorine to the extent of 0.2 to 2 percent, $R^- + O_2 \rightarrow RO_2^-$.

Abstractions by O_2, reaction (3) above, must have higher activation energy than those with F_2, but might be observable in more rigid polymers at higher temperatures. There is an outside possibility that many-lined radical spectra observed on heating polynuclear aromatic hydrocarbons [4] could have been due to reaction (3) rather than to simple pyrolysis.

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Mechanism of Peroxydation of Polymers

Adolphe Chapiro

Laboratoire de Chimie des Radiations du C.N.R.S., 92-Bellevue, France

The irradiation of polymers in the presence of air leads to polymeric hydroperoxides POOH and diperoxides POOP. When such irradiated polymers are used to initiate the polymerization of a monomer, hydroperoxides generate equal amounts of graft copolymer and homopolymer, whereas diperoxides only generate graft copolymer. This technique was used to study the peroxidation of various polymers under different irradiation conditions. It was found that polypropylene irradiated at temperatures ranging from 10 to 60 °C undergoes hydroperoxidation by a chain reaction. At 0 °C and below (in the vitreous polymer) polymeric radicals are formed but remain trapped. Poly(vinyl chloride) also leads to hydroperoxides when irradiated at 20 to 60 °C but no chain process develops below the glass transition temperature. Irradiation of the plasticized polymer leads to a hydroperoxidation by a short chain mechanism. It is concluded that the propagation of the hydroperoxidation chain, involving hydrogen abstraction by PO_2 radicals, only occurs above T_g when the mobility of polymeric segments is sufficient to ensure the interaction of PO_2 with neighboring molecules.

Polyethylene irradiated at room temperature chiefly generates diperoxides POOP. The chain hydroperoxidation only sets in above 35 °C. Below this temperature, recombination of PO_2 radicals occurs faster than hydrogen abstraction. The behaviour of polymers with respect to peroxidation is discussed and compared with that of low molecular weight model compounds.

Key words: Hydroperoxides versus diperoxides; influence of polymer phase on peroxidation; influence of temperature on peroxidation; peroxidation of polyethylene; peroxidation of polymers; peroxidation of polypropylene; peroxidation of poly(vinyl chloride).
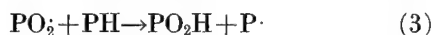
1. Introduction

When subjected to high energy radiation in the presence of oxygen most polymers undergo a peroxidation process. This reaction follows the classical scheme which can be written as follows:
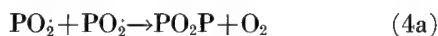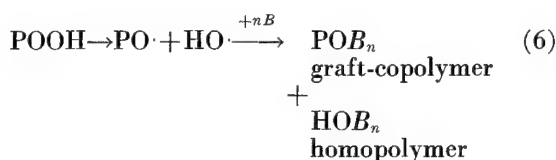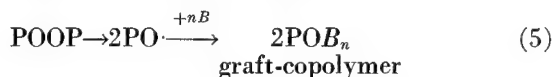
Initiation:

$$PH \rightsquigarrow P \cdot + H \cdot \qquad (1)$$

Propagation:

$$P \cdot + O_2 \rightarrow PO_2 \qquad (2)$$

$$PO_2 + PH \rightarrow PO_2H + P \cdot \qquad (3)$$

Termination:

$$PO_2 + P \cdot \rightarrow PO_2P \qquad (4)$$

$$PO_2 + PO_2 \rightarrow PO_2P + O_2 \qquad (4a)$$

According to this scheme, polymeric hydroperoxides POOH arise as a result of a chain reaction (with propagation steps 2 and 3) while diperoxides POOP (or peroxidic crosslinks) are formed in the combination of two radicals. When such polymeric peroxides are used to initiate a graft-copolymerization reaction, diperoxides generate only graft-copolymer, while hydroperoxides lead to equivalent amounts of graft-copolymer and homopolymer as shown below.

$$POOP \rightarrow 2PO \cdot \xrightarrow{+nB} \quad 2POB_n \qquad (5)$$
$$\text{graft-copolymer}$$

$$POOH \rightarrow PO \cdot + HO \cdot \xrightarrow{+nB} \quad POB_n \qquad (6)$$
$$\text{graft-copolymer}$$
$$+$$
$$HOB_n$$
$$\text{homopolymer}$$

It thus appears that a simple determination of the relative amounts of homopolymer versus graft-copolymer formed in the reaction provides information on the peroxidation process.

2. Experimental

Films of polymer 0.1 to 0.3 mm thick were subjected to different doses of gamma-rays in the presence of air at different temperatures. These films were thereafter sealed under vacuum in glass tubes containing a large excess of acrylonitrile. The tubes were then heated in a thermostat at temperatures usually ranging from 80 to 130°. The weight increase of the films as well as the amount of polyacrylonitrile homopolymer formed were determined as a function of time. Experiments were conducted with polyethylene [1, 2, 3],[1] polypropylene [2, 4] and poly(vinyl chloride) [5, 6]. Further experimental details are given in the original papers.

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[1] Figures in brackets indicate the literature references at the end of this paper.
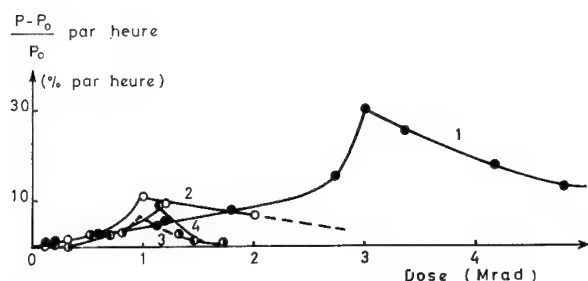
FIGURE 1. *Rate of grafting of acrylonitrile on preirradiated poly(vinyl chloride) films as a function of dose of gamma-rays [5, 6].*

curve 1:   20 °C; dose-rate 76 rads/min.
curve 2:   40 °C; dose-rate 73 rads/min.
curve 3:   60 °C; dose-rate 74 rads/min.
curve 4:   40 °C; dose-rate 7 rads/min.

3. Results and Discussion

Early experiments [1, 2] have shown that ir-radiation of polyethylene at 20 °C almost exclusively leads to diperoxides POOP whereas polypropylene under similar conditions generates hydroperoxides. This result was accounted for by assuming that step 3 does not occur in polyethylene at 20° but could take place in polypropylene on behalf of the labile tertiary hydrogens present in this polymer. These data conflicted, however, with the results of Bakh et al [7] who found that neither *n*-heptane nor isooctane (which contains tertiary hydrogens) underwent a chain hydroperoxidation when irradiated at room temperature. A chain reaction only developed above 40 °C.

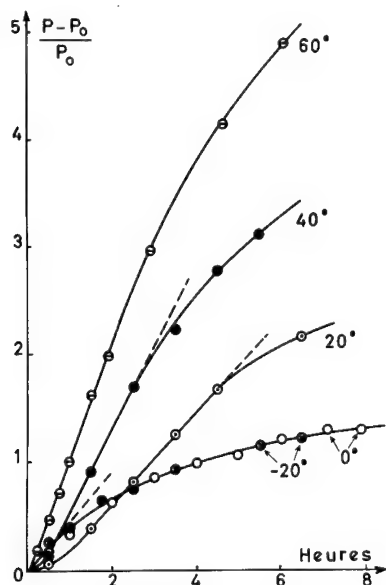Further work conducted with poly(vinyl chloride) [5] showed that this polymer generates hydro-

FIGURE 2. *Conversion curves of the graftcopolymerization of of acrylonitrile at 80°C onto polypropylene films preirradiated in air at different temperatures (as indicated on the curves).*

Dose of preirradiation: 0.3 Megarads [4].

peroxides under irradiation. However, the peroxide yield was found to be independent both of irradiation temperature and dose rate, thus precluding a chain reaction [6] (fig. 1).

A systematic study was conducted with poly-propylene. Films of this polymer were irradiated at temperatures ranging from -20 to $+60$ °C and acrylonitrile was thereafter grafted at 80° [4]. The conversion curves obtained after a dose of 3×10^5 rads are shown in figure 2. An Arrhenius plot of the initial rates is presented in figure 3.

It can be seen that for irradiations conducted between 20 and 60 °C the yield of peroxides (rate of grafting) steadily increases as required by the conventional chain peroxidation (steps 1 to 4). Below 0°, the yields are temperature independent and the shape of the conversion curves (fig. 2) denotes a change in mechanism, suggesting that in polymer films irradiated in this temperature range the grafting is initiated by trapped radicals. The
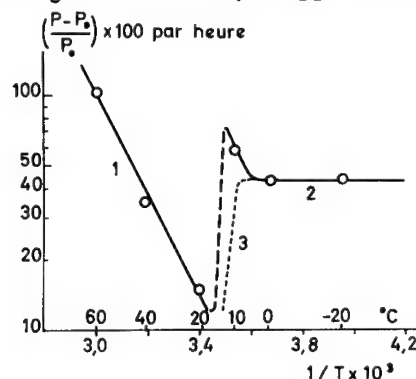

FIGURE 3. *Arrhenius plot of the initial rates of grafting of acrylonitrile onto polypropylene derived from the conversion curves shown in figure 2 [4].*

sudden change in mechanism appears more dramati-cally on figure 3. It is of interest to note that the glass transition temperature (T_g) of polypropylene is reported to be near 0°. The above results thus show that polypropylene irradiated above it T_g suffers a chain peroxidation the chain length of which steadily increases with temperature. Below T_g the polymeric radicals $P \cdot$ and $PO_2^\cdot$ cannot react for lack of mobility and they remain trapped in the polymer matrix.

These results were confirmed by further experi-ments with poly(vinyl chloride) (PVC). A hydro-peroxidation chain process does not develop in this polymer at room temperature since its T_g is 70 °C. The hydroperoxides POOH formed in this polymer presumably arise as a result of the recombination of trapped $PO_2^\cdot$ radicals with small, mobile radicals such as $H \cdot$ or HO_2:

$$PO_2^\cdot + H \cdot \longrightarrow PO_2H \qquad (7)$$

$$PO_2^\cdot + HO_2^\cdot \rightarrow PO_2H + O_2. \qquad (8)$$
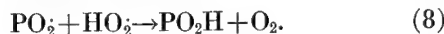
Experiments conducted with poly(vinyl chloride) films which had previously been "plasticized" with ca. 15 percent of chloroform showed that the yield of peroxides significantly increases. Figure 4 shows the

grafting rates as a function of dose of gamma-rays for the plasticized and unplasticized polymers. If one assumes that the rate of grafting is first order with respect to peroxide concentration (termination by radical burying) the data shown in figure 4 suggests a chain length of ca. 10 for the hydroperoxidation in the plasticized polymer.

In spite of the fact that polyethylene has a very low lying T_g(-40 °C) irradiation of this polymer at 20 °C chiefly leads to diperoxides, presumably via reaction step 4. By raising the irradiation temperature it was found [3] that a chain hydroperoxidation sets in above 35 °C. An Arrhenius plot of the data is shown in figure 5. At 70 °C the yield of peroxides exhibits a maximum. It is most probable that above this temperature a significant decomposition of the peroxides takes place during irradiation.
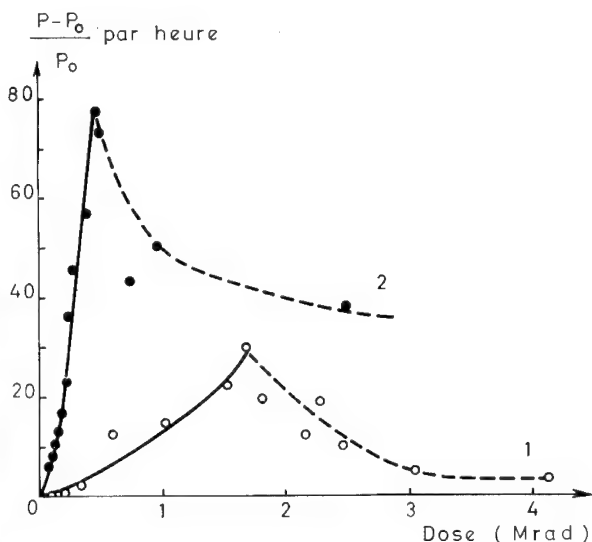
FIGURE 5. *Arrhenius plot of the rate of grafting of acrylonitrile onto polyethylene films preirradiated to a dose of 0.3 megarads at different temperatures* [3].

It should be further noted that reaction step 4 which involves the interaction of two polymeric radicals PO_2 is necessarily hindered by the low mobility of such radicals in the polymeric matrix. The corresponding reaction:

$$RO_2^{\cdot}+RO_2^{\cdot}{\rightarrow}RO_2R+R\cdot \qquad (9)$$
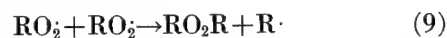
is much faster in a low molecular weight liquid than in a polymer and this accounts for the observation that polypropylene undergoes a chain hydroperoxidation under experimental conditions (temperature, dose-rate) under which isooctane does not. This emphasizes the fact that low molecular liquids cannot be taken as reliable model compounds for studying peroxidation of polymers at low temperatures.

4. Conclusions

The data presented in this work all pertain to radiation initiated peroxidation of polymers. However, since radiation peroxidation can be entirely accounted for by conventional free radical processes

FIGURE 4. *Influence of dose on the rate of grafting acrylonitrile onto poly(vinyl chloride).*

curve 1: unplasticized PVC;
curve 2: PVC plasticized with ca. 15 percent chloroform [6].

It should be pointed out that in this polymer the change in mechanism at ca. 35° only results from the competition involving reactions 3 and 4. Reaction 3 requires a higher activation energy and is thus favored at elevated temperatures. This competition is further affected by the concentration of $PO_2^{\cdot}$ radicals since these reactions are respectively of first and second order with respect to $(PO_2^{\cdot})$. It thus follows that the shift from the formation of peroxides by a single step reaction such as 4 to a chain hydroperoxidation (i.e., the break in the Arrhenius plot of figure 5) should depend on the radiation dose-rate. Such an effect was indeed observed by Saraeva [8] who found that the onset of the chain hydroperoxidation of heptane and other low molecular weight compounds was shifted to higher temperatures the higher the dose-rate. An Arrhenius plot of these data is schematically shown in figure 6.
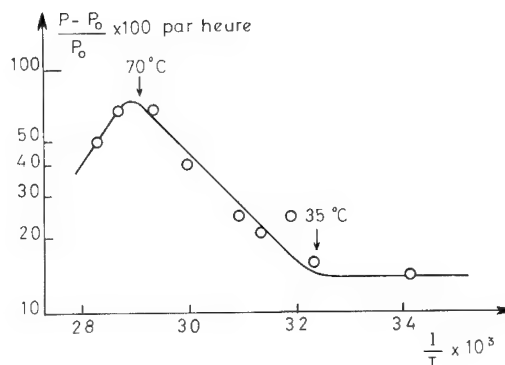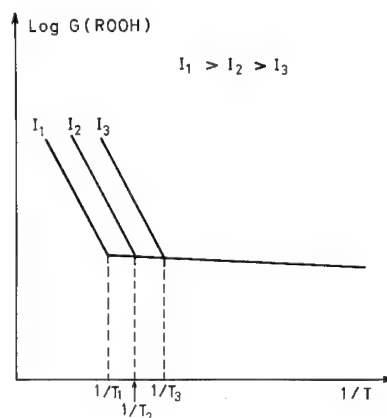
FIGURE 6. *Schematic plot of the radiation chemical yields of peroxides in low molecular weight hydrocarbons, based on data of Saraeva* [8].

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the conclusions derived from these results are more general in character and apply to any mode of initiation. It thus appears that when free radicals are generated in a polymer at temperatures above its glass transition point, a chain hydroperoxidation reaction may arise under appropriate conditions. The onset of the chain process is governed by a competition for peroxidic radicals which may either abstract hydrogen atoms from the polymer or combine. As in all chain reactions, higher temperatures and lower steady state concentrations of radicals favor the propagation step. Furthermore, since the combination of radicals occurs much faster in a mobile liquid than in a viscous polymer medium, the propagation step is favored in polymers and, hence, a chain hydroperoxidation process occurs more readily in a polymer than in a low molecular weight model compound treated under identical conditions.

Below the glass transition point of the polymer, most polymeric radicals remain trapped and thus accumulate. Peroxides may then still arise as a result of the combination of such trapped radicals with small radicals which are still mobile in the medium such as for instance $H\cdot$ and $HO_2^\cdot$. This leads to the formation of hydroperoxides by a one step reaction which is independent of temperature and of the rate of free radical generation.

5. References

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Discussion

J. H. Magill (University of Pittsburgh):

It is not clear to me why low molecular weight compounds cannot be used as model compounds to study reactions in polymers provided that experiments were conducted under isoviscous conditions. Compare,[1] for example, the viscosity data on polymers with small molecules. If the Stokes-Einstein relationship is applicable[2] to the molten polymeric state (C. R. Patrick, "Factors involved in the degradation of polymers in melts"), then the mobility of radicals would be comparable if viscosity (or diffusivity of polymer segments or molecules of the model compound) were the major rate determining factors.

A. Chapiro:

The peroxidation of a polymer in bulk is governed by two reaction steps: (1) propagation of the peroxidation chain in which a $PO_2^\cdot$ radical abstracts an $H\cdot$ atom from a neighboring RH groups; (2) termination of the chain by interaction of two polymeric radicals $PO_2^\cdot + PO_2^\cdot$ or $PO_2^\cdot + P\cdot$. Reaction (1) involves the interaction of a polymeric radical with a segment of a neighbor molecule. Such a process could perhaps be studied with low molecular weight model compounds since only a small displacement of polymer segments is required for the reaction. However, reaction (2) which requires the interaction of two free radical sites, attached to polymer molecules, with very low or even negligible mobility in the reaction medium and which must diffuse over fairly long distances to meet each other, cannot be compared with the reactivity of model compounds in a medium of same viscosity since the diffusibility of the small molecule is always much larger than that of the polymeric species. This is actually the reason, why under identical reaction conditions (and this includes identical viscosity) a polymer will suffer more severe peroxidation than a low molecular weight model compound; the lifetime of the free radicals and hence the chain length being much longer in the former system.

C. R. Patrick (University of Birmingham, England)

It has been suggested by Dr. Chapiro that in some degrading systems in melts the reactive free radical centres might be displaced more extensively as a consequence of chemical reactions than by physical diffusion. It has been acknowledged in my paper that under extreme conditions (of low molecular mobility) such displacements by reaction may proceed at a rate comparable with that of displacement by physical diffusion. Such conditions may readily prevail in reactions in rigid, partly crystalline or glassy polymeric matrices, or, indeed, in rubbery matrices at low temperatures. It remains my opinion that whilst such conditions may occur in polymeric melts, and that the possibility of their existence should not be overlooked, they will only infrequently justify the neglect of physical diffusion.

Any chemical reaction undergone by a free radical, be it a transfer reaction, of the type

$$R' + R''X \rightarrow R' + R''$$
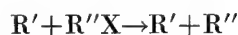
or a degradation step, in which the radical decomposes by the elimination of an olefin, is accompanied

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[1] See figure 3 in G. C. Berry and T. G. Fox, Advances in Polymer Science, 5, 261 (1968).
[2] There is no experimental evidence which suggests that it is widely applicable to highly anisotropic molecules over wide intervals of temperature and fluidity.

by a displacement of the reactive free radical centre. The length of the displacement in the first type of reaction must be greater than length of a chemical bond, but not by a large amount. A reasonable estimate would seem to be about $(3 \text{ to } 5) \times 10^{-8}$ cm, but most probably would lie close to the lower limit. In the second type of reaction the main chain of the free radical produced will be shorter than its progenitor by two carbon atoms. The displacement of the reactive centre in the second case is likely to be a little larger than in the first, and is probably about 5×10^{-8} cm, but is unlikely to exceed about 8×10^{-8} cm.

These displacements will take place on the average in an interval of time t_{chem}, given by $t_{chem} = (k_f[M])^{-1}$ for transfer reactions, and by $(t_{chem})_{av} = k_d^{-1}$ for elimination reactions, where k_f is the rate coefficient for the transfer reactions, $[M]$ is the molar concentration of centres at which the transfer reactions may take place, and k_d is the rate coefficient for the elimination of the olefin from the radical. Formally account should be taken of the possibility that the radical may undergo different reactions of either type. In most degrading systems of interest the rate of formation of olefin is likely to exceed that of the transfer reactions, although it is evident from the nature of the products formed in the thermal degradation of some polymers that the transfer reactions may proceed at rates that are significant compared with the elimination reactions.

As stated in the paper, it is unlikely that rate coefficients for elimination of olefins from radicals will exceed $10^{14} \exp[-25000/RT]$ s^{-1} (R = 1.9873 cal deg^{-1} mole^{-1}). Thus even at 450 °C, k_d is unlikely to exceed 3×10^6 s^{-1}. It would seem that in many polymeric melts in which degradation takes place, the diffusivities, even of the larger radicals, would be greater than above 10^{-9} cm^2 s^{-1}. In a time $t_{chem} = k_d^{-1} = 3 \times 10^{-7}$ s., the root mean square diffusive displacement $(= [6Dt_{chem}]^{1/2})$ is about 5×10^{-8} cm. This is to be compared with estimate of about 5×10^{-8} cm. for the displacement of the reactive centre resulting from the chemical reaction. At lower temperature for example 300°, k_d is unlikely to exceed 5×10^4 s^{-1}. In the case of polystyrene at this temperature, D is about 10^{-10} cm^2 for molecular weights of interest. The r.m.s. displacement resulting from translational diffusion during the average time for one chemical act of eliminating an olefin is therefore 11×10^{-8} cm., and larger than the displacement of the radical centre as a result of the chemical process.

We conclude that in general displacements due to diffusion occur at a rate that is at least comparable with the rate of displacement by chemical processes, and diffusion will normally have an important, if not dominant role, in determining the rate of encounter, and therefore of reaction, between macroradicals in polymer melts. It should be noted that this view is reinforced by the fact that in our calculations we have considered only the least favourable class of radical-radical reactions, namely by the encounter of two large radicals, rather than by, for example a large radical and a small radical, and that we have used as estimated for the diffusivities values that relate to the diffusion of centres of mass, which may be smaller than those relating to the diffusion of segments.

Oxidative Degradation of Polymers and Organic Compounds Via Unimolecular Decomposition of Peroxy Radicals
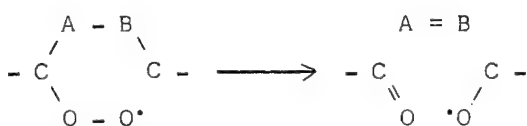
Jean Marchal

Centre de Recherches sur les Macromolecules—C.N.R.S., 6 rue Boussingault, 67-Strasbourg, France

Autoxidation of various polymers and organic compounds is shown to include, already at room temperature, chain scissions involving unimolecular decomposition of secondary and tertiary peroxy radicals. Rate and product data are consistent with a scheme including a six-membered ring transition state leading to three fragments, one of them being an alkoxy radical. This oxidative degradation scheme at room temperature does not correspond to a known mechanism.

Key words: 1,4-dioxane; kinetics; mechanism; organic compound; oxidative degradation; peroxy radical isomerization; poly(ethylene oxide); polymer; polypropylene; poly(propylene oxide); polystyrene; polytetrahydrofuran; room temperature.

1. Introduction

Experiments in the very early stages of autoxidation of various polymers and organic compounds were done at room temperature by using γ-irradiation for initiation. Whether the radiation-induced reactions take place in dilute solution or on the pure compound, the results show that chain scissions occur without any induction period. This oxidative degradation is described by means of a unimolecular decomposition process of secondary and tertiary peroxy radicals leading to three fragments, schematically written:

$$
\begin{array}{ccc}
\begin{array}{c} A - B \\ / \qquad \backslash \\ - C \qquad\quad C - \\ \backslash \qquad / \\ O - O^{\bullet} \end{array}
& \longrightarrow &
\begin{array}{c} A = B \\ / \qquad \backslash \\ - C \qquad\quad C - \\ \backslash\backslash \qquad / \\ O \quad {}^{\bullet}O \end{array}
\end{array}
$$

The alkoxy radicals thus formed are responsible for propagation and termination of chain reactions of autoxidegradation. Intramolecular propagation leads to small fragments. A=B can be an ethylenic compound, in which case it works as an efficient radical scavenger.

2. Radiation-induced Autoxidation by γ-Irradiation of Dilute Solutions

To study the reactions involved in the autoxidation of organic compounds, it is very important to ensure that the process used for initiation does not also induce decomposition of the reaction products. Many results obtained by using conventional initiation processes such as thermal, uv and redox free radical generators are questionable in this respect.

This difficulty is overcome when γ-rays are used to produce active species for the initiation of the autoxidation. Since the amount of energy which is dissipated by collisions leading to ionization by the Compton effect is proportional to the electron density of the irradiated medium, it is clear that the relative amount of this energy absorbed by each constituent is proportional to its electron density and weight fraction. The result is that a relatively large accumulation of the products of the autoxidation is possible before the limiting effect of their decomposition by γ-irradiation becomes appreciable. In fact, this direct effect is still negligible when secondary reactions of the products of the autoxidation with free radical initiators become noticeable.

For the same reason, it is possible to irradiate a mixture in which the dilution of an organic solute is such that the yield of free radicals resulting from its radiolysis by the direct effect of γ-irradiation can be neglected compared to that resulting from the indirect effect due to the H atom abstraction from the solute by active species produced by the solvent radiolysis. As a very important consequence, the solute does not undergo any chain scission which would be due to the direct effect of γ-irradiation.

A good illustration of the use of those properties in oxidation reactions is given by the hundreds of investigations devoted to the quantitative determination of the yield of free radicals and "molecular" products which is basic to the understanding of the water radiolysis. To determine the radiolytic yield of reducing radicals, one way, reviewed by Baxendale [1],[1] is to use oxygen as a radical scavenger and to determine the radiation yield $G(H_2O_2)$ of hydrogen

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[1] Figures in brackets indicate the literature references at the end of this paper.

peroxide. Another way, reviewed by Bielski and Allen [2], is to use the radical scavenger made of oxygen+organic additive such as ethanol or ethylene glycol (Ahmad et al. [3]) and to determine the total peroxide yield.

Added to the possibility of working in ordinary vessels, at any temperature and with very well determined absorbed dose rates, those properties make the radiation-induced initiation by γ-irradiation a very versatile and powerful technique to study autoxidation reactions, mainly in dilute solutions.

3. Oxidative Degradation Measurements in Dilute Solution

The experiments reviewed here are done in our laboratory with polymers in dilute solution by using radiocobalt γ-rays to induce oxidative processes at 25 °C. The oxidative degradation occuring during autoxidation has been determined by viscometry and gas phase chromatography.

Viscometric properties of polymer coils are not modified by hydroperoxide formation on the macromolecules since it does not change their overall dimensions. On the other hand, they are very sensitive to random chain scissions which are produced by the oxidative degradation. The quantitative determination of the yield of random chain scissions is possible from the experimental value of the limiting viscosity number $[\eta]$, when the initial molecular weight distribution of the polymer sample and the Mark-Houwink law $[\eta]=kM\alpha$ in the same solvent are known. We used the Saito [4]-Kotliar [5] method. Irradiation cells were glass tubes topped by a capillary viscometer (fig. 1).

Viscometric properties of polymer coils are not significantly modified by fragmentation when the oxidative degradation concerns the end groups of macromolecules or by minute fragmentation when intramolecular propagation follows random chain scissions. Gas phase chromatography has been used to identify and to determine the yields of the low molecular weight products of those scissions.

The yield of hydroperoxides was determined in irradiated aqueous solution by using titanic ions in sulfuric acid medium as described by Pobiner [6].

4. Autoxidative Degradation of Poly(ethylene oxide)

Experiments are carried out on a standard polymer sample Hoechst "Polyaethylenglykol 15,000" $M_w=15,000\pm500$: light scattering measurement; $M_n=12,500\pm500$: dosage of alcohol end groups. Autoxidation of the polymer is radiation-induced in aqueous or chloroform solutions. Absorbed doses are determined by taking the standard $G(Fe^{3+})=15.5/100$ eV for the Fricke dosimeter in O,8N H_2SO_4.

Good oxygenation conditions of the irradiated solutions exist when the rate of the autoxidation is

FIGURE 1. *Irradiation cell (viscometer).*

not dependent on the liquid level in the cells, the oxygen pressure and absorbed dose rate being constant. They were determined in experimental tubes as follows, for the ratio free surface/liquid volume ≥ 1 cm^{-1}:

$I<400$ rads·min^{-1} for concentration $1\leq c\leq4$ g·100 cc^{-1} in chloroform solutions saturated with oxygen in open air,

$I<50$ rads·min^{-1} for concentration $2\leq c\leq6$ g·100 cc^{-1} in aqueous solution saturated with oxygen under $P_{(O_2)}=2$ kg·cm^{-2}.

4.1. Random Chain Scissions

Kinetic results obtained in chloroform solution by Gugumus [7] and in aqueous solution versus pH by Crouzet [8] have been reviewed in a first paper [9].

Viscometric measurements show that chain scissions are formed without any induction period. By using the Saito-Kotliard method, it has been possible to demonstrate that the rate of formation of chain scissions is not dependent on the initial M_n value of the sample. This is the proof that observed chain scissions are randomly distributed along polymer chains. Knowing the initial molecular weight distribution function of the samples, which is very close to the Schulz-Zimm one, the average number $\bar{x}$ of random chain scissions per macromolecule is deduced from the value of the ratio $[\eta]/[\eta]_0$ of the limiting viscosity number after and before irradiation.

Kinetic results obtained in each solvent show that the average number $\bar{x}$ of random chain scissions per
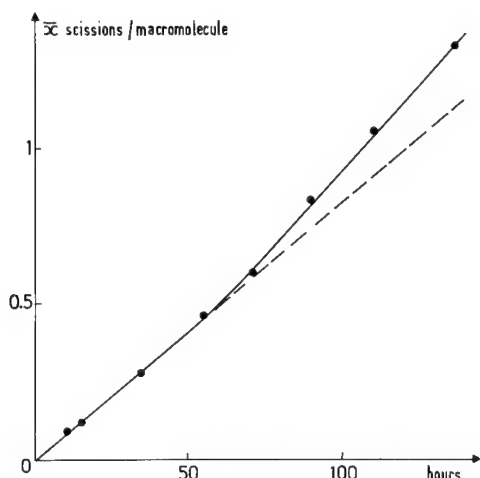
FIGURE 2. *Random chain scissions in aqueous solution.*

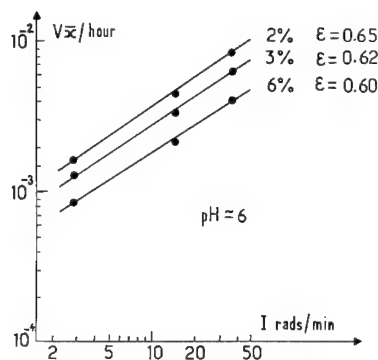$c = 2g.100cc^{-1}$, $I = 36$ rads.mn^{-1}, natural pH~6.

FIGURE 3. *Experiments in water.*

macromolecule is proportional to the absorbed dose in the early stages of radiation-induced autoxidation at 25 °C. An example is given in figure 2. One can see on this figure that the effects of secondary reactions responsible for the increase of the rate of formation of random chain scissions begin to be noticeable when the effects of the primary random chain scission process are already relatively important. One can also see from figures 3 and 4 that the initial rate of formation of random chain scissions per initial macromolecule obeys a law $V_{\bar{x}} = kI^{\diamond 0,5}$ in each solvent, ϵ decreasing as the polymer concentration increases.

The initial rate of formation of random chain scissions per unit volume of solution $V_{\text{scissions}}$ is given by the relation:

$$V_{\text{scissions}} = V_{\bar{x}} \cdot c \cdot \frac{N_0}{M_n}$$

where N_0 is Avogadro's number.

4.2. Related Chemical Groups

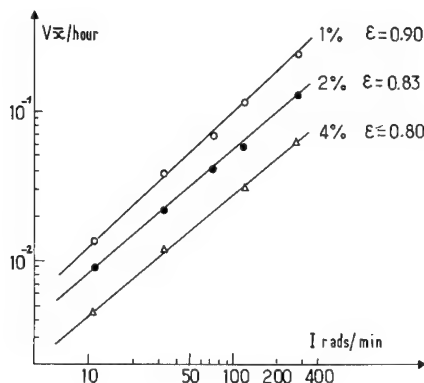The related chemical groups are formate ester or primary alcohol at the end of the fragments and

FIGURE 4. *Experiments in chloroform.*

formaldehyde. In dry chloroform solution, Gondet et al. [10] established that the very fast side reaction of formaldehyde with alcohol end groups of initial macromolecules explains the accumulation of hemiformal groups identified by Gugumus without any measurable induction period. In aqueous solutions, formate esters tend to be hydrolysed.

4.3. Minute Fragmentation

In both solvents, the initial rates of formation of those chemical groups including formaldehyde are higher than the initial rate of random chain scissions determined by viscometry. This result has been explained by Decker [11] who, using gas phase chromatography, identified 9 low molecular weight compounds which are also produced without any measurable induction period. These are small fragments produced by intramolecular propagation and termination of the autoxidative degradation of the polymer. They are: formic acid, ethylene glycol, its formate esters and aldehyde, diethylene glycol, its formate esters and aldehyde.

Since gas phase chromatography is used to analyse the oxidation products, it has been necessary to verify that none of these products are formed by thermal decomposition of peroxides in the apparatus. This has been done by two ways. The first is that the increase of the temperature of the injection chamber from 120 °C to 250 °C is followed neither by a change of the yields of the detected products or by the detection of new compounds. The second is that during freeze-drying of the polymer from the irradiated aqueous solutions, the low molecular weight products are removed and recovered with the water. Furthermore no signal appears on the chromatogram of solutions made with the dried oxidized polymer in fresh water.

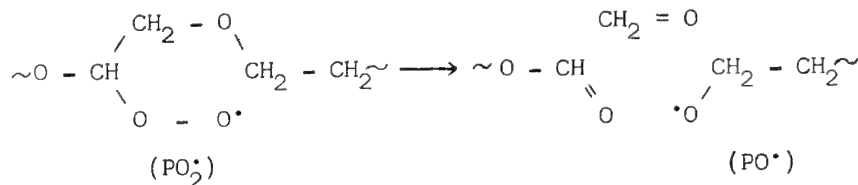These results, their kinetic treatments and mechanisms have been recently detailed [11].

4.4. Unimolecular Decomposition of α-Alkoxyalkylperoxy Radicals

It has been pointed out in the first part of this paper that the homolysis of peroxides by direct

effect of γ-irradiation must be negligible in the early stage of the radiation-induced autoxidation because their concentration is too low.

Furthermore, the increase in the yield of chain scissions, which is due to the post-effect initiated by the thermolysis of peroxides at 25 °C, remains very low when, after irradiation, the solutions are kept at this temperature in the dark. This result confirms

that the spontaneous peroxide decomposition is not able to explain the initial rate of formation of chain scissions during the autoxidation of the polymer at 25 °C.

Our rate and product data on several polymers are consistent with a unimolecular decomposition of alkylperoxy radicals $PO_2^{\cdot}$ such as:

According to this scheme which, admittedly, does not correspond to a known mechanism, the primary alkoxy radicals $P_1O^{\cdot}$ would be responsible for propagation of the autoxidative degradation of the polymer.

Consequently, bimolecular reactions of two $PO_2^{\cdot}$ radicals would be less probable. Therefore we have constructed a scheme for the autoxidegradation of the polymer at 25 °C where termination reactions are assumed to occur by bimolecular reactions of P_1O radicals.

In aqueous solutions, $PO_2^{\cdot}$ and $P_1O^{\cdot}$ radicals being unable to react with the solvent, the scheme of the autoxidative degradation of the polymer is simpler.

Initiation*

$H_2O \xrightarrow{\gamma}$	$OH^{\cdot}$	$V_i = K(G_{OH} \cdot I)$

Transfer and Propagation

$OH^{\cdot} + PH \rightarrow H_2O + P^{\cdot}$ (k_2)

$P^{\cdot} + O_2 \rightarrow PO_2^{\cdot}$ (k_3)

$PO_2^{\cdot} + PH \rightarrow PO_2H + P^{\cdot}$ (k_4)

$PO_2^{\cdot} \rightarrow P_1O^{\cdot} + P_2-O-CHO + HCHO$ (k_5)
  (unimolecular decomposition)

$P_1O^{\cdot} - PH \rightarrow P_1OH - P^{\cdot}$ (k_6)

Termination**

$2P_1O^{\cdot} \rightarrow P_1OOP_1$ (negligible) (k_7)

$\quad\quad \rightarrow P_1=O + P_1OH$ (disproportionation) (k_8)

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* Crouzet [8] found that initiation by O_2^- radicals is not possible because they do not react with the polymer. This was already found by Bakh [14] for ethers.

** According to our scheme, $P_1O^{\cdot}$ are primary alkoxy radicals: their recombination (reaction 7) must be negligible.

4.5. Kinetic Equation for Random Chain Scissions

From the above theoretical scheme of free-radical chain reactions where intramolecular propagation reactions are disregarded, the rate of the formation of random chain scissions is:

$V_{\text{scissions}}$

$$= k_5[PO_2^{\cdot}] - \tfrac{1}{2}k_7[P_1O^{\cdot}]^2$$

$$= K G_{OH} \cdot I \left(1 - \frac{1}{2}\frac{k_7}{k_7 + k_8}\right) + \left(\frac{K G_{OH} \cdot I}{k_7 + k_8}\right)^{1/2} k_6[PH]$$

$$= \alpha KI + \beta(KI)^{1/2}$$

αI corresponds to termination reactions, the rate of which is equal to the rate of initiation under steady-state conditions. $\beta(KI)^{1/2}$ is the rate of propagation by $P_1O^{\cdot}$ radicals.

(a) α Values

In aqueous solution as well as in chloroform solution, this kinetic equation for random chain scissions is in good agreement with experimental results which lead to α values independent of the polymer concentration c:

H_2O: $\alpha = 2.8 \pm 0.2$ $2 \leq c \leq 6 \text{ g} \cdot 100cc^{-1}$

Crouzet [8]

$CHCl_3$: $\alpha = 6.2 \pm 1$ $1 \leq c \leq 4 \text{ g} \cdot 100cc^{-1}$

Gugumus [7]

Within experimental errors, α values are close to G_{OH} of water radiolysis and to G_R for chloroform radiolysis.

H_2O: $G_{OH} \cdot = 2.74 \pm 0.08$

Bielsky and Allen [2]

$CHCl_3$: $G_R \cdot = 7 \pm 2$

see [15] reviewed by Gugumus [7]

These results are consistent with $k_7 \ll k_8$, meaning that the termination of autoxidegradation of the polymer is done by disproportionation of the primary alkoxy radicals $P_1'O^{\cdot}$. As was already mentioned Decker [11] found that low molecular weight $P_1'O^{\cdot}$ radicals are formed by intramolecular propagation of the autoxidegradation of the polymer. These alkoxy radicals $P_1'O^{\cdot}$ are: $HO-CH_2-O^{\cdot}$, $HO-CH_2-CH_2-O^{\cdot}$ and $HO-CH_2-CH_2-O-CH_2-CH_2-O^{\cdot}$. From the study of the autoxidegradation of the first homologous

polymers of the series, di- and tri-ethylene oxide α,ω-glycols, Decker [11] found that the smaller the molecular size of these alkoxy radicals, the higher is their efficiency for termination reactions. This may be understood in terms of mobility of active species. The efficiency of HO–CH$_2$–O$\cdot$ in disproportionation reaction leading to formic acid is specially high. It can be explained by the mesomeric effect:

$$HO—CH_2—O\cdot \rightleftharpoons O=CH—OH$$
$$\overset{.}{H}$$
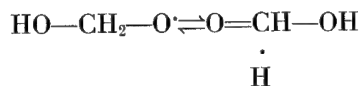
These results also support the assumption that termination reaction without chain scission which may involve 2PO$_2^{\cdot}$ radicals or PO$_2^{\cdot}$+HO$_2^{\cdot}$ (or RO$_2^{\cdot}$ in the case of chloroform solutions) are negligible. If this was not so, we would have found $\alpha < G_{OH}$. or $\alpha < G_R$.

(b) β Values

In both solvents, experimental β values for random chain scissions vary linearly with the polymer concentration c. According to the kinetic equation for $V_{scissions}$, this result indicates that all the radicals capable of initiating the autoxidation of the polymer are trapped by the solute in the range of concentrations used. This result also demonstrates the existence of chain reaction of oxidative degradation.

4.6. Autoxidegradation as Main Chain Reactions at 25 °C

To conclude, the main feature of this work is that the termination of the free-radical chain reactions of the autoxidation of poly(ethylene oxide) induced at 25 °C seems to be performed by alkoxy radicals produced by the unimolecular decomposition of α-alkoxyalkylperoxy radicals PO$_2^{\cdot}$ and not by bimolecular reactions of these radicals because those reactions appear to be less probable; this is contrary to usual concepts for ether autoxidation.

According to this conclusion, the main chain reactions are those of "autoxidegradation", hydroperoxidation acting only as side chain reactions regenerating P$\cdot$ macroradicals (retardation reactions).

We are pursuing this work in order to confirm and to describe the unimolecular decomposition of PO$_2^{\cdot}$ radicals which has been postulated here.

Recently Decker [12] got the proof that the oxygen atom in formaldehyde is coming from the polymer chain and not from oxygen gas. This result which demonstrates that formaldehyde is produced by fragmentation of the polymer chains has been obtained by using almost pure $^{18}O_2$ gas instead of $^{16}O_2$ to perform the radiation-induced autoxidation at 25 °C. Experiments were done in dry chloroform solutions where isotopic exchange reactions are negligible. The results were followed by ir spectroscopy on the irradiated solutions. The upper part of figure 5 corresponds to experiments in the presence of $^{16}O_2$. It shows that two absorption bands are present in the region of $\nu_{C=O}$ groups. $\nu \simeq 1755$ cm^{-1} has been attributed [7] to ester groups formed in the polymer chain —O—C— and $\nu \simeq 1725$ cm^{-1} to the

$$\overset{\|}{O}$$

remaining free formaldehyde and to formate esters. If all carbonyl groups formed during autoxidation in the presence of $^{18}O_2$ have been labelled with ^{18}O, the result would have been a shift of $\simeq -30$ cm^{-1} of the
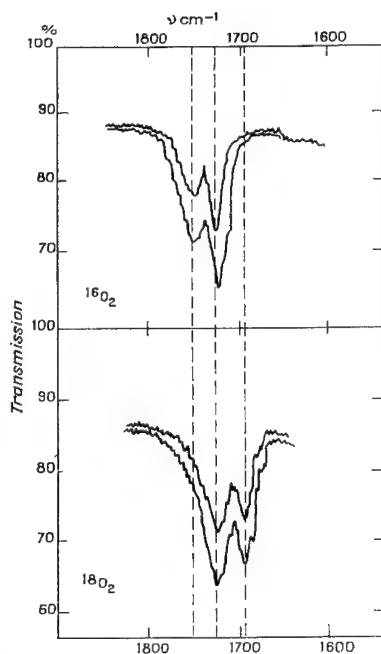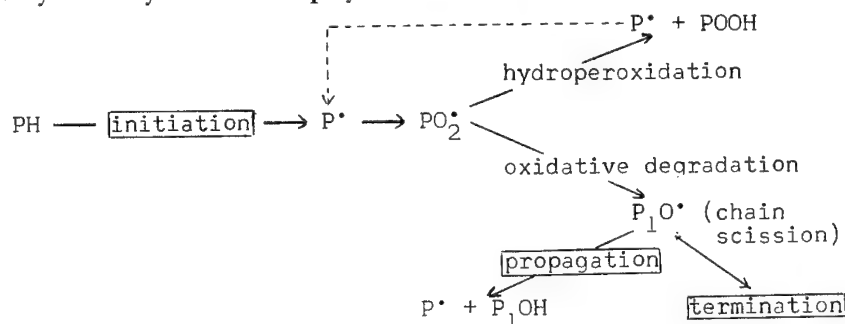
FIGURE 5. *Irradiated solutions of poly(ethylene oxide) in chloroform, 50 and 96 hours, I = 125 rads.mn^{-1}.*

entire ir spectrum without any noticeable change of its shape. The lower part of figure 5 which corresponds to the same experiments in the presence of $^{18}O_2$ shows that this is not the case, indicating clearly that one kind of carbonyl groups is not labelled with ^{18}O. The disappearance of the previously $\nu \simeq 1755$ cm^{-1} band is explained by the shift of $\simeq -30$ cm^{-1} of $\nu_{C=O}$ of esters in the chain. The appearance of a band $\nu \simeq 1695$ cm^{-1} is attributed to the shift of $\nu_{C=O}$ of formate esters. Thus $\nu \simeq 1725$ cm^{-1} corresponds to the absorption of labelled esters in the chains and to

$$-O-\underset{\underset{O^{\textbf{·}}}{|}}{CH}-CH_2-O-CH_2-CH_2\sim \longrightarrow$$
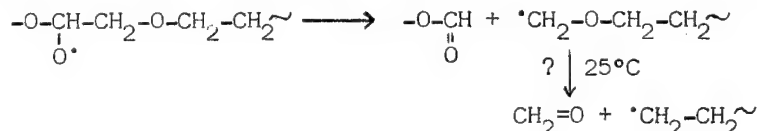
To be kinetically valid, this hypothesis requires that the PO· radicals be produced without any induction period. Considering the conventional concepts of autoxidation, this can only be achieved by the bimolecular reaction that we have so far neglected:

$$2PO_2^{\textbf{·}} \rightarrow 2PO\textbf{·} + O_2$$
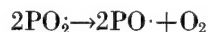
This hypothesis also requires that these PO· radicals disappear only by unimolecular decomposition and that the $\sim CH_2-CH_2-O-CH_2^{\textbf{·}}$ radicals thus formed be in turn too unstable, at 25 °C in solution satured with oxygen, to lead to any reaction other than their decomposition producing formaldehyde.

This research is actually undertaken with polymer samples containing hydroperoxide groups. They are prepared by recovering from aqueous irradiated solutions by freeze-driing in order to eliminate all low molecular weight products. Then, hydroperoxide groups are decomposed, in fresh dilute solutions, by different ways: thermolysis, uv radiation and redox systems.

Another way to get information is to use ESR spectroscopy to observe free radicals produced in a liquid flow. We are investigating this technique in order to obtain direct informations concerning kinetics and lifetimes of $PO_2^{\textbf{·}}$ and alkoxy radicals. The determination of the orders of the disappearance rates of these species would provide conclusive evidence.

Finally, by using the same radiation-induced technique, we are extending this work, by searching for other compounds undergoing oxidative degradation, at 25 °C, which can be interpreted as we did for poly(ethylene oxide). Until now, we found that this is the case for *p*-dioxane, poly(propylene oxide), polytetrahydrofuran, polypropylene and polystyrene. The experiments mentioned below were done in chloroform solution and also in the pure state for *p*-dioxane.

nonlabelled formaldehyde. This has been confirmed by the fact that the addition of a weak amount of water to irradiated solutions in the presence of $^{16}O_2$ or $^{18}O_2$ was enough to induce the decrease of the absorption $\nu_{C=O} \simeq 1725$ cm^{-1} because the hydration reaction of formaldehyde is very fast without noticeable hydrolysis of formate esters.

Since formaldehyde is produced by fragmentation of polymer chains, it might also be possible to interpret its formation as the result of the decomposition of α-alkoxy-alkylalkoxy PO· radicals:

$$-O-\underset{\underset{O}{\|}}{CH} + \textbf{·}CH_2-O-CH_2-CH_2\sim$$
$$? \downarrow 25°C$$
$$CH_2=O + \textbf{·}CH_2-CH_2\sim$$

5. p-Dioxane

For this cyclic dimer of ethylene oxide, autoxidegradation leads to formaldehyde and ethylene glycol monoformate ester with similar yields [16]. By using $^{18}O_2$, Decker [13] reached the same conclusion concerning the formation of formaldehyde as for linear poly(ethylene oxide). One can see in figure 6 that autoxidation of *p*-dioxane in the presence of $^{16}O_2$ leads to only one $\nu_{C=O}$ absorption band $\simeq 1725$ cm^{-1} and that this absorption band is split into two bands $\simeq 1725$ cm^{-1} and $\simeq 1695$ cm^{-1} when autoxidation has been induced in the presence of $^{18}O_2$. It was thus easier to interpret this result: the remaining absorption band $\simeq 1725$ cm^{-1} corresponds to unlabelled formaldehyde and the other absorption to the ^{18}O labelled carbonyl group of formate esters.
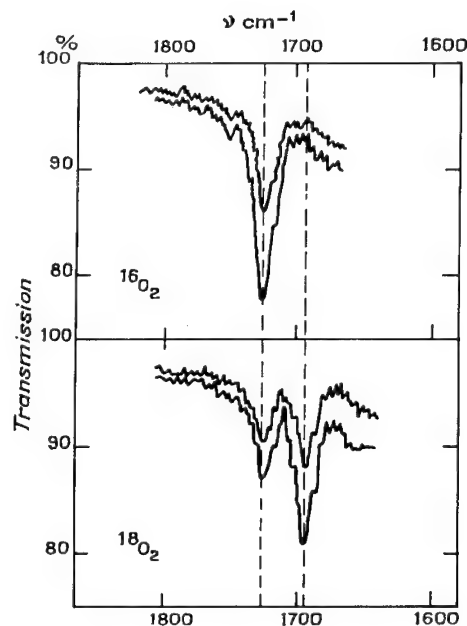
FIGURE 6. *Irradiated p-dioxane, 87 and 159 hours, I = 125 rads.mn^{-1}.*

Furthermore, this result is qualitatively the same whether the radiation-induced experiments are done in dilute chloroform solution or with the pure compound. This is the proof that the observed degradation is not due to the direct effect of γ rays on peroxides, which confirms the general statement given in the general introduction.
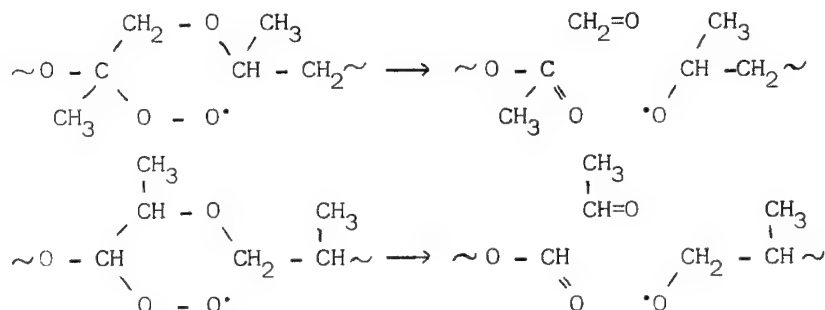
6. Poly(propylene oxide)

Radiation-induced autoxidation in dilute chloroform solution has been studied on a regular head to tail but atactic polymer sample (Union Carbide poly(propylene oxide)α,ω-glycol NIAX 4025, $M_n =$ 3,200).

Gondet [17] found that all conclusions concerning poly(ethylene oxide) are valid for this homologous polymer. But the number of low molecular weight compounds produced by intramolecular propagation of the autoxidative degradation is higher because monomeric units contain an asymetric carbon atom.
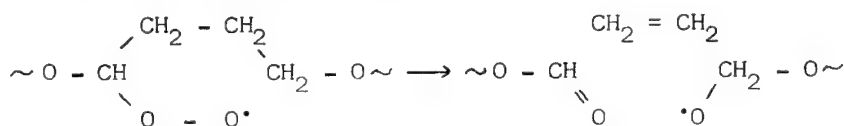
The postulated intramolecular decomposition of $PO_2^\cdot$ radicals is able to explain the yields of formaldehyde and acetate ester groups and the yields of acetaldehyde and formate ester groups, depending whether the $PO_2^\cdot$ are secondary or tertiary peroxy radicals:

$$
\begin{array}{c}
\sim O - C \left\langle \begin{array}{c} CH_2 - O \\ \\ CH_3 \quad O - O^\cdot \end{array} \right. \left. \begin{array}{c} CH_3 \\ CH - CH_2 \sim \end{array} \right. \longrightarrow \sim O - C \left\langle \begin{array}{c} CH_2=O \\ \\ CH_3 \quad O \end{array} \right. \quad ^\cdot O \left. \begin{array}{c} CH_3 \\ CH - CH_2 \sim \end{array} \right.
\end{array}
$$

$$
\begin{array}{c}
\sim O - CH \left\langle \begin{array}{c} CH_3 \\ CH - O \\ \\ O - O^\cdot \end{array} \right. \left. \begin{array}{c} CH_3 \\ CH_2 - CH \sim \end{array} \right. \longrightarrow \sim O - CH \left\langle \begin{array}{c} CH_3 \\ CH=O \\ \\ O \end{array} \right. \quad ^\cdot O \left. \begin{array}{c} CH_3 \\ CH_2 - CH \sim \end{array} \right.
\end{array}
$$

The yield of formaldehyde is higher than the yield of acetaldehyde as expected from usual properties of H atom abstraction by free radicals.

7. Polytetrahydrofuran

A polymer sample, $M_w \simeq 30,000$, has been prepared by SbCl$_5$ cationic-induced polymerization in dry diethylether at low temperature. Thomassin [18] found that ethylene is formed without any induction period during the radiation-induced autoxidation of the polymer in chloroform solutions at 25 °C. This result may be described as follows:

$$
\sim O - CH \left\langle \begin{array}{c} CH_2 - CH_2 \\ \\ O - O^\cdot \end{array} \right. CH_2 - O \sim \longrightarrow \sim O - CH \left\langle \begin{array}{c} CH_2 = CH_2 \\ \\ O \end{array} \right. \quad ^\cdot O \quad CH_2 - O \sim
$$

In this case, it is interesting to point out that the low molecular weight product of the unimolecular decomposition of $PO_2^\cdot$ is an ethylenic compound which can work as an efficient free radical scavenger.

8. Polypropylene

Thomassin [18] also found that propylene is formed during the radiation-induced autoxidation of an atactic polymer-sample in chloroform solution at 25 °C. The same oxidative degradation process has been proposed to explain this result:

$$
\sim CH_2 - C \left\langle \begin{array}{c} CH_3 \\ CH_2 - CH \\ \\ CH_3 \quad O - O^\cdot \end{array} \right. \left. \begin{array}{c} CH_3 \\ CH_2 - CH \sim \end{array} \right. \longrightarrow \sim CH_2 - C \left\langle \begin{array}{c} CH_3 \\ CH_2 = CH \\ \\ CH_3 \quad O \end{array} \right. \quad ^\cdot O \left. \begin{array}{c} CH_3 \\ CH_2 - CH \sim \end{array} \right.
$$
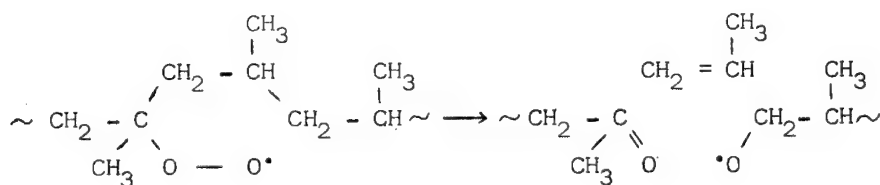
9. Polystyrene

Like the above listed polymers, polystyrene undergoes oxidative degradation during radiation-induced oxidation in dilute chloroform solution at 25 °C. Samples used have been obtained by anionic polymerization. Abadie [19] determined the initial rate of random chain scissions by using the viscometric method of Kotliar-Saito and found that styrene is produced with the same initial rate. Those results support the assumed process:
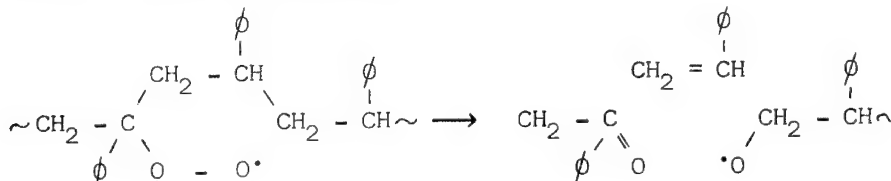
Styrene works as a very efficient radical scavenger.

The main differences compared with the behavior of poly (ethylene oxide) are:

• The oxidative degradation is not a chain reaction: $V_{scissions}$ is proportional to the absorbed dose and does not depend on the polymer concentration $3 \leq c \leq 8 \ g \cdot 100cc^{-1}$.

• Consequently there are no small fragments which would be due to intramolecular propagation.

Detailed results will soon be published [20].

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Discussion

C. F. Cullis (The City University, London):

One of Dr. Wall's objects in arranging the present Symposium was, I think, to seek "bridges" between those working on systems in which only simple well-defined chemical entities are involved and those studying the reactions of more complex species such as polymers. In this connection, Dr. Marchal's work underlining the importance of the unimolecular decomposition and rearrangement of peroxy radicals during the oxidation of polymers at room temperature finds some parallel in studies of the gaseous oxidation of simple hydrocarbons and related compounds at considerably higher temperatures. Thus, it has been possible to acquire in recent years [A. Fish, Quart. Rev. Chem. Soc. **18**, 243 (1964)] a greatly increased understanding of the modes of gaseous decomposition of alkyl peroxy radicals as well as a realisation of the importance of rearrangement reactions some of which are at least formally analogous to those suggested by Dr. Marchal. However, it is fairly generally agreed that, during the combustion of hydrocarbons, unimolecular reactions of alkylperoxy radicals become important relative to bimolecular reactions only at rather high temperatures. Although, from other than energetic points of view, the conditions existing in the condensed phase will be more conducive to the occur-

rence of the breakdown and rearrangement of peroxy radicals, it is perhaps a little surprising that the favourable entropy factors should be able to outweigh the unfavourable energy factors and thus enable unimolecular decomposition of such radicals to take place quite extensively at room temperature.

J. Marchal:

The comment of Professor Cullis opens the discussion by raising the question that I was anticipating.

First, may I outline some points concerning the aim of my paper to this symposium.

–The object of this paper has been very precisely to report experimental results, for polymers and low molecular weight compounds, which are inconsistent with the usual assumption that unimolecular decomposition reactions of peroxy radicals are energetically difficult and are thought not to occur at room temperature.

–The fundamental question of the proposal of a mechanism which would be able to justify such a scheme at room temperature was not treated in this paper because the necessary theoretical information on peroxy radical chemistry has not yet been developed. It was thought that reference only to results obtained for hydrocarbon oxidation at high temperature would not be helpful.

I should add that we have been working on this basic question from a theoretical point of view. I am pleased to have the opportunity to reply to Professor Cullis before the printing of the proceedings of this symposium by referring to the beginning of the publication of a series of papers which propose a way to reach an answer.

In the first paper [1] of this series, a three step mechanism is proposed to interpret the unimolecular decomposition scheme of peroxy radicals at room temperature.

–The first step is a peroxy radical isomerization reaction leading to the introduction of a peroxide linkage in the molecular backbone. This reaction is based upon charge transfer interaction:

–The second step is the radical-induced decomposition of the peroxidic bond:
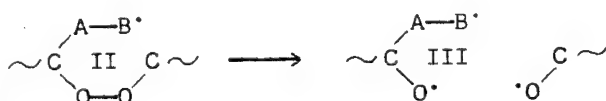
–The third step is the homolytic decomposition of AC bond of the diradical III:

This three step mechanism is detailed in a communication [2] at the IUPAC conference on Chemical Transformations of Polymers in Bratislava (to be published).

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R. E. Florin (National Bureau of Standards):

In Dr. Marchal's paper, the number of identified products corresponding to the mechanism is impressive. Regarding the program for observing radical intermediates, the ESR spectrum of radical P⋅ has been well characterized in flow mixing experiments on $TiCl_3$, H_2O_2 and polyoxyethylene in aqueous solution [1]. Another radical spectrum of more ambiguous origin is observed as well, perhaps $\sim OCH_2\dot{C}HOH$ or $[\sim OCH-CH_2]^+$, having g = 2.0024, doublet a = 18.7 Oe, triplet a = 22.2 Oe. The peroxy radical PO_2 spectra are well known, with high g and no hyperfine structure. The alkoxy radical g value and hyperfine splitting will be hard to predict. Although $OH⋅$ [2], $CH_3CH_2O⋅$ [3], and $C_6H_5O⋅$ [4] ESR spectra are reported, the former two are broadlined, anisotropic polycrystalline or glassy spectra with little detail and doubtful identification, while the latter, though exact, may be irrelevant because of extensive electron delocalization.

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J. Marchal:

Dr. Florin refered to ESR measurements of free radicals produced on poly(ethylene oxide) in flow mixing experiments. May I give our results on the same subject [1].

The second radical spectrum described by Dr. Florin is observed in acidic but not in neutral media (the reagent being neutralized by NH_4OH and the Ti^{4+} ions being complexed with EDTA). The spectrum of the radical P⋅ produced by random H atom abstraction along the polymer chain $\sim O-\dot{C}H-CH_2-O\sim$ is then the only one which is observed.

The origin of the second radical spectrum observed in acidic medium is neither of the two species mentioned by Dr. Florin, but is $\sim$O–CHOH–$\dot{C}H_2$.

The formation of this radical, in acid catalysed reactions, can be rationalized on the basis of the decomposition of radical P· and the isomerization of the radical $\sim$O–$\dot{C}H$–CH_2OH thus formed. It is proposed that the isomerization reaction proceeds in the manner described for corresponding radicals of vinyl ethers [2]:

$$\sim CH_2-CH_2-O\ -CH_2-\dot{C}H-O\sim$$
$$\quad H_3O^+$$
$$\xrightarrow{} \sim CH_2-CH_2-OH + HO-CH_2-\dot{C}H-O\sim$$
$$\quad H_3O^+$$
$$\sim O\dot{C}-H-CH_2-OH \xrightleftharpoons{} \sim O-CHOH-\dot{C}H_2$$
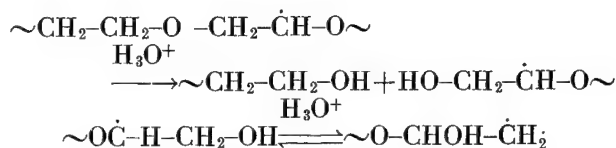
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Mechanisms of Oxidation of Polyolefins below 150 °C

Frank R. Mayo

Stanford Research Institute, Menlo Park, Calif. 94025

This paper applies what we have learned about oxidations of simple aliphatic hydrocarbons below 150 °C to oxidations of bulk polyolefins. The principal difference between these groups is due to the production of initiating radicals in pairs and to the greatly restricted mobilities of all radicals. Data are given for the efficiency of initiation by di-*t*-butylperoxy oxalate of the oxidation of atactic polypropylene at 45 °C and for the effect of peroxide concentration on efficiency and kinetic chain length. The following other topics are discussed: chain propagation and geminate and statistical termination by alkylperoxy radicals, nonterminating reactions of two tertiary alkoxy radicals, formation and reactions of alkoxy radicals, sensitivity of oxidation products to further oxidation, intramolecular propagation of alkylperoxy radicals, and the question of the formation of carbonyl groups in oxidations of polyolefins.

Key words: Alkoxy radicals; carbonyl compounds; chain initiation; chain propagation; chain termination; kinetics; oxidation; peroxy radicals; polyolefins; polypropylene.

1. Introduction

Whether we wish to prevent oxidation of polymers, to accelerate their destruction, or to control the introduction of functional groups by oxidation, better understanding of the mechanisms seems essential for efficient progress. From our experience with liquid-phase oxidations of simple hydrocarbons, the competing reactions that determine the rates and products of oxidation of polyolefins below 150 °C have been deduced. The difficulties in measuring these competitions, and the failure of nearly all published work to meet the conditions necessary to obtain basic information are discussed. These discussions assume that polyolefin radicals are almost always generated close together in pairs, that their mobility is so restricted in bulk polymers that efficiencies of initiation may approach zero, and that for every pair of effective initiating radicals, there must be one, and only one, pair of terminating groups. While light and ionizing radiation may cleave chains directly, in oxidations of saturated aliphatic hydrocarbons the difference between oxidations in the light and in the dark is assumed to depend on the ways in which pairs of radicals are generated, not on what happens to them subsequently.

2. Efficiency of Production of Polymer Radicals

We have used di-*t*-butylperoxy oxalate (DBPO) to initiate oxidations of atactic polypropylene [1][^1] at 45°. This initiator has a convenient half life and

[^1]: Figures in brackets indicate the literature references at the end of this paper.

after several half lives the *t*-butoxy radicals can be recovered quantitatively and the number of chains initiated determined. In one experiment with 0.615 mole DBPO/kg atactic polypropylene at 45°, 73.5 percent of the total potential *t*-butoxy radicals were recovered as di-*t*-butyl peroxide, 14.8 percent as *t*-butanol, and 11.7 percent as *t*-butoxy groups bound to polymer (as *t*-butyl chloride after cleavage of the ether with anhydrous hydrogen chloride). The di-*t*-butyl peroxide measures the *t*-butoxy radicals which were wasted in a cage combination reaction. The 14.8 percent of *t*-butanol measures the total hydrogen abstracted from the polymer (polymer radicals produced) by *t*-butoxy radicals. The 11.7 percent ether measures the *t*-butoxy groups wasted by near-cage reactions of *t*-butoxy and polymer radicals. Thus only the *t*-butanol in excess of the ether, here 3.1 percent, corresponds to polymer radicals available for starting oxidation chains and to the efficiency of initiation. Here, 73.5 percent of the potential *t*-butoxy groups were lost in cage combination and 88 percent of the remainder were wasted in near-cage ether formation.

The efficiency of initiation increases with increasing temperature or with addition of small amounts of solvents, both of which facilitate separation of caged radicals. Knowledge of the efficiency of initiation is necessary for establishing kinetic chain lengths and the proportions of oxidation products corresponding to chain termination.

3. Chain Propagation and Termination Reactions of Alkylperoxy Radicals

In the presence of sufficient oxygen, all the substrate is brought into reaction by alkylperoxy or

alkoxy radicals. Propagation reactions of the resulting alkylperoxy radicals in oxidations of alkanes are relatively difficult. The activation energy for propagation of t-alkylperoxy radicals with tertiary aliphatic hydrogen atoms is about 16 kcal/mole [2, 3], with secondary hydrogen atoms, about 17 kcal/mole. Reactions of peroxy radicals with primary hydrogen atoms (methyl groups) are negligible below 150°. The only termination known for two tertiary peroxy radicals is

$$2RO_2^. \rightarrow R_2O_2 + O_2$$
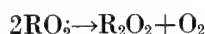
for which the activation energy is about 9 kcal/mole [3]. Competing with this termination is the non-terminating reaction
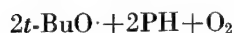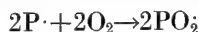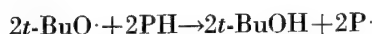
$$2RO_2^. \rightarrow 2RO^. + O_2$$

with the same or a slightly higher activation energy [4]. In the absence of peroxide decomposition by heat, light, or transition metals, this latter reaction is the principal source of alkoxy radicals, which are considerably more reactive than alkylperoxy radicals and can attack methyl groups. With t-butylperoxy radicals in liquid isobutane at 80°, about 10 nonterminating interactions occur for each terminating interaction. The fraction of nonterminating interactions presumably decreases, as for alkoxy radicals, as the viscosity of the medium increases.

Terminations that involve one or more primary or secondary peroxy radicals are much faster than those for two tertiary peroxy radicals,[5] have an activation energy close to that for diffusion, show a deuterium isotope effect for α-substitution [5, 6], and give mostly an alcohol and an aldehyde or ketone as termination products. Hiatt [4] showed that interactions of such radicals are almost always terminating in liquid systems below 100° and hence give few, if any, alkoxy radicals.

4. Kinetics of Oxidation

The oxygen consumed in initiation and termination alone in the oxidation of polypropylene (PH) is directly proportional to the number of initiating radicals:

$$2t\text{-BuO}^. + 2PH \rightarrow 2t\text{-BuOH} + 2P^.$$

$$2P^. + 2O_2 \rightarrow 2PO_2^.$$

$$2PO_2^. \rightarrow \text{termination products} + O_2$$

$$2t\text{-BuO}^. + 2PH + O_2$$
$$\rightarrow 2t\text{-BuOH} + \text{termination products}$$

We are now concerned with the *additional* oxygen absorption, all associated with chain propagation. When the two radicals that terminate are descendants of the same initiating pair (geminate radicals), then this oxygen absorption is first order in rate of initiation and radical pairs. When the two radicals that terminate are descendants of different initiating pairs (statistical combination), then this oxygen absorption is one-half order in rate of initiation.

The distinction between geminate and statistical combination is important. The former is probably associated with short kinetic chains that may be difficult or impossible to inhibit. The latter is probably associated with much longer kinetic chains that may be easy to inhibit. Besides indicating the direction of further research on inhibitors, the distinction is important for correlating initiation with oxygen absorption and for devising and interpreting accelerated aging tests.

Table 1 summarizes some recent experiments which illustrate our difficulties in determining the kinetics of oxidation. The major difficulty arises from an increase in efficiency of initiation with the concentration of DBPO, probably due to the plasticizing effect of DBPO and its decomposition products. Some interesting but useless coincidences result: The total oxygen absorption is closely proportional to the concentration of initiator but to the one-half power of the number of initiating radicals. However, the oxygen absorption in chain propagation alone (last line) is not between one-half and first order as expected, but is about 0.3 order. We conclude that the increasing concentration of DBPO which results in increasing efficiency of initiation also favors termination of oxidation chains more than it favors propagation of chains. This conclusion suggests that oxygen absorption in propagation should be measured at various concentrations of DBPO in mixtures adjusted with solvent so that the efficiency of initiation is constant.

5. Reactions of Alkoxy Radicals

Alkoxy radicals are important in polymer oxidations because (except for radiation) they provide the only free radical route to chain cleavage below 150°. At higher temperatures, or in the presence of light or transition metals, alkoxy radicals may arise from decompositions of peroxides, but in the dark below 100° they are formed mostly from interactions of *two tertiary* peroxy radicals. Thus, chain cleavage in the dark at moderate temperatures depends on the proportions of secondary and tertiary peroxy radicals that are present, the competition between terminating and nonterminating reactions of two tertiary peroxy radicals, and the competition between propagation and cleavage of the resulting alkoxy radicals. Whereas some of these ratios are known for simple alkanes, I know of no published values for polymers.

TABLE 1. *Oxidations of polypropylene at 45°*
(Concentrations in moles/kg)

[DBPO]$_0$	0.317	0.671	1.269
Efficiency (e), %	6.1	10.8	21.2
$\Delta P^. = 2e$[DBPO]$_0$ [a]	0.0387	0.145	0.538
ΔO_2 [b]	0.153	0.296	0.563
ΔO_2/[DBPO]$_0$	0.48	0.44	0.44
$\Delta O_2/(\Delta P^.)^{1/2}$	0.778	0.777	0.768
$(\Delta O_2 - e$[DBPO]$_0)/(\Delta P^.)^{1/2}$	0.68	0.59	0.40

[a] Total P$^.$ radicals generated.
[b] Total O$_2$ absorbed.

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Some results on the oxidation of cumene are relevant. Most of the chain termination in the oxidation of cumene involves methylperoxy radicals, present in very low concentrations compared with cumylperoxy radicals, but much more reactive in chain termination. The methylperoxy radicals come from cleavage of cumyloxy radicals, formed from nonterminating interactions of cumylperoxy radicals. Participation of methylperoxy radicals was established by Traylor and Russell [7]; they found that addition of t-butyl hydroperoxide accelerated the ABN-initiated oxidation of cumene by converting methylperoxy and cumyloxy radicals to t-butyl-peroxy radicals. At low temperatures (which discourage cleavage of cumyloxy radicals) and low rates of oxidation (where radical interactions are less probable), Hendry showed that methyl termination is largely eliminated [8].

In oxidations of polypropylene and poly(1-butene), alkylperoxy radicals presumably attack mostly the tertiary hydrogen atoms and the resulting tertiary peroxy radicals terminate relatively slowly. However, any accompanying nonterminating interactions produce alkoxy radicals, and cleavage of the latter radicals then can produce primary alkyl and alkyl-peroxy radicals. The latter accelerate chain termination, slow the oxidation, and reduce the nonterminating interactions that produce cleavage and more primary radicals.

6. Implications of Other Oxidations

Among alkanes, oxidation of isobutane [3] is the best understood. The unique characteristics of this oxidation illustrate the serious difficulties encountered in studying oxidations of all other alkanes and polyolefins. The principal products from isobutane below 200°, depending on conditions, are t-butyl hydroperoxide, t-butanol, di-t-butyl peroxide, acetone, and oxidation products of methyl radicals. Except for products from methyl radicals, all of these products are surrounded by unreactive methyl groups and are reasonably resistant to further oxidation. Thus, oxidation of isobutane can be carried to 5 to 10 percent conversion without much interference from secondary oxidations. Whereas the methyl radicals from cleavage cause some complications, t-butoxy radicals are stable enough that effects of cleavage and the resulting methyl radicals are not serious below 50°.

However, t-butoxy radicals are unique in that they contain only methyl groups, which are difficult to cleave. Hence, *all other* alkoxy radicals cleave more easily than t-butoxy [9, 10], and complications from the (usually) primary cleaved alkyl radicals greatly affect the rates and products of reaction. (Phenyl radicals are less easily lost than methyl radicals; hence the oxidation of cumene is also relatively simple.)

Whenever primary or secondary alcohols or aldehydes or ketones are primary oxidation products, their further oxidation presents complications. From labeling experiments in the oxidation of cyclohexane at 150°, the relative reactivities of cyclohexane, cyclohexanol, and cyclohexanone are found to be in the ratio 1:22:29 on a molecular basis, 1:264:87 on a per-active-hydrogen basis [11]. (The per-hydrogen results are probably a little high because they neglect the reactivity of all other hydrogen atoms.) These differences should be larger at lower temperatures. Thus, secondary reactions of primary products may complicate analyses as well as their interpretation, even at conversions as low at 0.1 percent. In polymers where oxidation depends on autocatalysis or photolysis of previous products, secondary reactions may be further exaggerated because of high local concentrations of oxidation products that do not diffuse.

Aldehydes, formed by oxidation of primary radicals from cleavage of alkoxy radicals, can be particularly troublesome. Benzaldehyde is about 100 times as reactive as toluene [12] toward t-butyl-peroxy radicals at 30° and probably still more reactive compared to isobutane. Moreover, the benzoylperoxy radical appears to be 100 to 1000 times as reactive as alkylperoxy radicals in chain propagation [13] and presumably less selective. The aliphatic aldehydes are comparable [13]. Further, aldehydes in general seem able to initiate oxidation chains.

As a result of all these secondary reactions, the oxidation of any pure alkane or saturated polyolefin soon begins to involve the relatively very reactive primary and secondary products, hydroperoxides, alcohols, aldehydes, and ketones, and distinctions due to differences in starting hydrocarbon will tend to disappear earlier at lower temperatures. As a warning to chemists who are concerned with measurements of rate constants in oxidations of hydrocarbons, I propose the approximation: at about 1 percent conversion in the oxidation of any saturated aliphatic hydrocarbon at any chosen temperature, the apparent rate constants for chain propagation and termination in the oxidizing mixture will be largely independent of the starting hydrocarbon. For the reasons given above, this principle fails for the oxidation of isobutane. It does not apply to alkenes and alkylbenzenes, which are reactive enough to give long kinetic chains and to protect their primary oxidation products.

7. Intramolecular Chain Propogations

The most quoted evidence for intramolecular chain propagation in oxidation is that of Rust [14]. Oxidation of 2,4-dimethylpentane with 35 psi of oxygen at 115 to 120° gave an 89 percent yield of hydroperoxide with an estimated 90 percent of the total oxidation product containing oxygen on both the 2- and 4-carbon atoms. 2,3-Dimethylpentane and 2,4-dimethylhexane gave less but still substantial disubstitution.

Chien, Vandenberg, and Jabloner [15] obtained an oxidized isotactic polypropylene from an ABN-initiated oxidation in chlorobenzene solution at 100°. They determined the hydroperoxide content,

and by infrared and other studies concluded that it contained no isolated, but only sequences of, hydroperoxide groups and that there was a strong tendency toward intramolecular propagation. Although they may eventually prove to be partly correct, their conclusions are not justified. Their kinetic chain lengths suggest that their oxidation product may have contained as many terminating as hydroperoxide groups, but they give only hydroperoxide, no total oxygen, determinations. A simple calculation shows that if each polymer peroxy radical has an equal chance of propagating intramolecularly or of terminating, most of the hydroperoxide groups would still be in sequences: one quarter would be isolated; one quarter would be in pairs, and one half would be in sequences of three or more. I see no plausible mechanism that would account for the reported absence of isolated hydroperoxide groups.

Dulog and Kern have studied the oxidations of isotactic and amorphous polypropylenes [16] and poly(1-butene)s [17] in solution. Although differences were found in the rates of autocatalytic oxidations of the polypropylenes at 120 to 140° and attributed to a greater tendency toward intramolecular propagation in the isotactic polymer, in ABN-initiated oxidations at 70° no significant differences were found. At 70°, the indicated kinetic chain lengths were 1 to 3. Yields of hydroperoxide were about 30 percent on the oxygen absorbed.

Apparently no one has so far obtained kinetic chains in oxidations of polyolefins in solution that were long enough to justify good yields of hydroperoxides in sequences.

8. Carbonyl Groups in Oxidations of Polyolefins

Some workers have reported the presence of carbonyl groups in oxidation products of polypropylene in the dark and some have reported the absence of such groups. I am seeking further examples. Dulog and Kern [16] report that carbonyl groups were absent in the products of their autocatalytic oxidations at 120 to 140°. Chien et al. [15] reported a similar result in their ABN-initiated oxidations at 100°. However, Stivala and Reich [18] have used carbonyl groups as the principal measure of rate of oxidation of isotactic polypropylene films at 120 to 150°. Further, Adams [19] has just reported finding several kinds of carbonyl groups in the thermal oxidation of polypropylene, although more hydroperoxide and less carbonyl were found in oxidations after 380 hours at 63° than after 2 hours at 138°. Our own work at 45° provides ample infrared evidence of carbonyl groups. Since these experiments lasted only 6–7 hours in the dark, the carbonyl groups can hardly come from the decomposition of hydroperoxides but must represent cleavage and termination products.

I have no satisfactory explanation for these discrepancies. The few cited results suggest that carbonyl groups are more likely to be found in

oxidations of bulk than of solution polypropylene. I also point out that alcohol and hydroperoxide groups, particularly when they are in 1,3-positions, may obscure carbonyl absorption by hydrogen bonding or hemiketal formation.

9. Conclusions

Essentially all of the published work on the oxidation of polyolefins fails to provide the needed kinds of fundamental data for one or more of the following reasons. (1) It was carried out in solution and hence neglects the important cage and viscosity effects in bulk polymers. (2) The rate of initiation was unknown. (3) The conversion was too high and secondary reactions interfered. (4) It was carried out at temperatures too high to be relevant to practical problems. (5) It reports activation energies that are inconsistent with simple primary reactions, meaning that the authors are dealing with an unrecognized change in mechanism. (6) The rate of oxidation was high enough or the sample was thick enough that effective oxygen concentrations in the polymer were diffusion-dependent and unknown. (7) To the extent that the oxygen supply varies in different regions of the polymer, so may the rates, products, and mechanisms of oxidation vary.

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10. References

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Discussion

F. H. Winslow (Bell Telephone Laboratories):

In section 1 of his paper, Mayo indicated that both thermal and photooxidations of saturated aliphatic hydrocarbons proceeded primarily by radical mechanisms. But, there is abundant evidence that chain cleavage by a Norrish II (non radical) process is a major mechanism in the oxidative photo-degradation of polyethylene. In addition, the hydroperoxide intermediates, so important in thermal oxidations of hydrocarbons, are absent or at least their presence has not been demonstrated in photo-oxidations. In fact, our studies have shown that hydroperoxides, formed by autoxidation of polyethylene, decompose so fast on exposure to 3000 Å radiation that significant concentrations cannot develop during photooxidation. Some Norrish I or other radical reactions undoubtedly occur in photo-oxidations at moderate temperatures but radical-chain reactions are absent or at least insignificant since: (1) photo-oxidations of hydrocarbons at room temperature or below are essentially non-autocatalytic and exhibit no induction period. (2) Chain terminating anti-oxidants such as hindered phenols have no significant effect on the degradation rate.

D. W. Brown (National Bureau of Standards):

Polymers of 3,3,3-trifluoropropene; 2,3,3,3-tetrafluoropropene; and 3,3,4,4,5,5,5-hepta-fluoropentene-1 were aged at 225 °C in air and in preevacuated tubes. At various times samples were dissolved in hexafluorobenzene and the intrinsic viscosities were determined at 29.8 °C. In 87 hours none of the samples heated in preevacuated tubes changed in intrinsic viscosity. With the air-aged specimens, the intrinsic viscosity of poly (3,3,3-trifluoropropene) decreased rapidly whereas values for the other two polymers showed little change. Presumably, the relatively great resistance of poly-(2,3,3,3-tetrafluoropropene) to oxidation is due to its lack of a tertiary hydrogen atom. Our speculation as to the cause of the resistance to oxidation of poly(3,3,4,4,5,5,5-heptafluoropentene-1) is connected with its solubility. Although this polymer has a hydrocarbon backbone, it is soluble in perfluoro-hexane, whereas neither of the other polymers is so soluble. In acetone, the polypropenes are soluble and the polypentene insoluble. Possibly, the long fluoro-carbon side chain associates with the hydrocarbon backbone and confers fluorocarbon-like behavior, in oxygen as well as in solution.

Polymer-Gas Reactions (Air Pollutants: NO₂ and SO₂) as Function of Pressure, UV Light, Temperature, and Morphology—A Survey

H. H. G. Jellinek

Clarkson College of Technology, Potsdam, N.Y. 13676

Reactions of various polymers, such as polystyrene and its stereo-specific isomers, butyl-rubber, nylon, etc., with nitrogen dioxide and sulfur-dioxide were studied by the author and co-workers in recent years. Mechanisms of these reactions in presence of these gases, near ultra-violet light and oxygen were elucidated. Diffusion phenomena have also been investigated and their importance has been pointed out. More recently, work has been initiated on the influence of polymer morphology on degradation of polymers in presence of these gases, near uv radiation and oxygen. Unexpected effects have been observed during chain scission near room temperature. Thus, for instance, isotactic polystyrene of various crystallinities, as far as extent and type are concerned, show marked differences in their degradation characteristics. Thus, for instance, crystalline polymers show faster degradation than amorphous ones, which seems to be contrary to expectations. However, this phenomenon can be explained in quite a consistent manner. The importance of all these reactions in connection with air pollution is briefly discussed.

Key words: Air pollutants; butylrubber, degradation, effect of NO₂; degradation, effect of morphology; effect on polymers of NO₂, SO₂, air and U.V. light; nylon, degradation, effect of NO₂; polymer-gas reactions; polystyrene, atactic, degradation, effect of NO₂; polystyrene, diffusion of NO₂ and degradation; polystyrene, isotactic, degradation, effect of SO₂.

1. Introduction

We have studied reactions between polymer films and gases such as NO_2, SO_2, O_2 (air), irradiated with uv light, in recent years. The kinetics and mechanisms were elucidated. We have also started investigations on the effect of polymer morphology (extent of crystallinity) on the stability of various polymers under such "environmental" conditions. Quite unexpected results were obtained as function of morphology, contrary to expectations, which, however, after some reflection, appear to be quite reasonable and can be at present, qualitatively explained.

The films which were used for these investigations were usually quite thin (ca. 20 μm to 25 μm), this eliminates diffusion phenomena. However, for thicker films, diffusion has to be considered and we have done some research in this direction. The significance of all this work is not only of fundamental but is also of practical value with respect to air pollution.

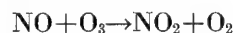## 2. Some Reactions of NO₂ and SO₂

It will be opportune to discuss briefly some reactions of these gases with O_2 and small hydrocarbons in presence of ultraviolet light; these processes are relevant to the reactions with polymers which will be discussed in this paper.

NO_2 is an odd electron compound, hence very reactive—a strong oxidizing agent. It reacts in presence and absence of oxygen (in the dark) with unsaturated hydrocarbons such as cyclohexene,

1–3 butadiene and 1-hexene. It is suspected that amongst the reaction products, there are small amounts of powerful (effective in parts per billion) eye irritants of the type

$$\begin{array}{ccc} R & & R \\ \diagdown & & \diagup \\ & C=C & \\ \diagup & & \diagdown \\ NO_2 & & R \end{array}$$
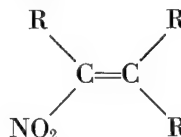
In presence of uv light, NO_2 reacts very strongly with hydrocarbons forming aldehydes, ketones and epoxides [1].[1] It is suspected that ozone is formed during some of these reactions,

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + NO + M \rightarrow NO_2 + M$$

$$O + NO_2 \rightarrow NO + O_2$$

$$O + NO_2 + M \rightarrow NO_3 + M$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$NO + NO_3 \rightarrow 2NO_2$$

$$NO + O_3 \rightarrow NO_2 + O_2$$
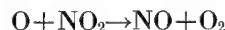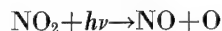
If this is the case, much of the deterioration of elastomers (e.g. rubber) will be due to ozone. Thus olefins (e.g. $CH_3CH=CHCH_3$) can react with

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[1] Figures in brackets indicate the literature references at the end of this paper.

ozone as follows,

$$CH_3CH=CHCH_3 + O_3 \rightarrow CH_3\overset{H}{\underset{OO\cdot}{\overset{|}{C}}}-\overset{\dot{O}}{\overset{|}{C}}HCH_3$$

$$\rightarrow CH_3\overset{H}{\overset{|}{C}}OO + CH_3CHO$$
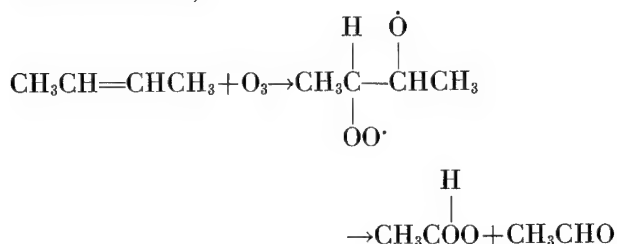
The reaction of SO_2 with saturated and unsaturated hydrocarbons in presence of uv light leads to sulfinic acid; Dainton and Ivin [2] suggested the following reaction sequence,

$$SO_2 + h\nu \rightarrow SO_2^*$$

$$SO_2^* \rightarrow SO_2$$

$$SO_2^* + SO_2 \rightarrow SO_2 + SO_2$$

$$SO_2^* + RH \rightarrow SO_2 + RH$$

$$SO_2^* + RH \rightarrow RSO_2H$$

Also here ozone may be one of the reaction products,

$$SO_2 + 2O_2 \overset{h\nu}{\longrightarrow} SO_3 + O_3$$

Thus NO_2 and SO_2 are quite aggressive under various conditions; it is not surprising that polymers are affected by these gases.

3. Reaction of NO_2 and SO_2 with Polymers [3]

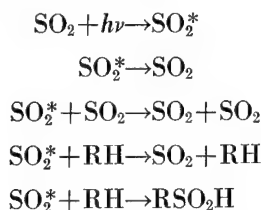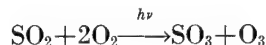A survey was first made of the effect of SO_2 and NO_2, respectively, in absence or presence of O_2 and near uv radiation on various polymer films. The high vacuum apparatus will not be described here. Two classes of polymers stand out quite distinctly with respect to main chain scission due to these gases: (1) saturated polymers and (2) unsaturated polymers (elastomers). The latter are very much more reactive, than the former, as is to be expected. The saturated polymers show a variety of different reactivities according to their chemical structure. Polycarbonate, for instance, is fairly stable, polyesters undergo chain scission and cross-linking. All reactions were carried out at about 30 °C.

Some reactions were studied in detail and a short survey will be given here, indicating their most prominent features.

4. Reaction of NO_2 with Atactic Polystyrene Films [4].

High vacuum apparatuses were used in this and subsequent investigations in conjunction with medium pressure uv light sources; all light below about 2800 to 3000 Å was cut off by pyrex glass. The reaction vessels, arranged in a circle around this light source, were thermostated. Devices were incorporated in the reaction vessels so that films on glass-slides could be exactly located with respect to the light source. At the end of each film exposure, the film was evacuated to prevent any continuation of the reaction. Intrinsic viscosities were measured at definite time intervals and eventually converted to number average chain lengths.

It is of importance to note that there exists an equilibrium between the monomer (NO_2) and its dimer (N_2O_4). Below about 1 cm Hg of NO_2 pressure, this equilibrium can be neglected as it lies for low pressures practically completely on the side of the monomer, which is the reactive species,

$$N_2O_4 \rightleftharpoons 2NO_2$$
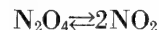
The partial pressure of NO_2, P_{NO_2}, is given by,

$$P_{NO_2} = [(K_p^2 + 4K_p P_{total})^{1/2} - K_p] \qquad (1)$$

Here, K_p, is the equilibrium constant and $P_{total} = P_{NO_2} + P_{N_2O_4}$ the total gas pressure. Films prepared by casting from solution [4] were exposed over a range of temperatures from 25 to 55 °C and pressures from 11 to 60 cm (total). The results are expressed in degrees of degradation $\alpha = \dfrac{1}{DP_{n,t}} - \dfrac{1}{DP_{n,0}}$ versus exposure time, t. A typical plot for 30 cm NO_2 as a function of temperature (dark reaction, no air) is shown in figure 1. $\overline{DP}_{n,t}$ and $\overline{DP}_{n,0}$ are the number average chain lengths at time t and $t=0$, respectively. The Arrhenius energy of activation for this reaction amounts to ca. 12.2 kcal/m and the pre-exponential factor is about 2×10^3 to 1×10^4 hr^{-1}.

The films were not treated especially during their formation as far as their morphology is concerned and they are most likely amorphous. At this stage of the work, morphology was not investigated.

Quite an interesting and noteworthy phenomenon was observed during the initial stages of the degradation reaction. Intrinsic viscosity measurements require straight lines for their plots of η_{sp}/c versus c. However, after relatively short exposure times of the films, straight lines could not any more be
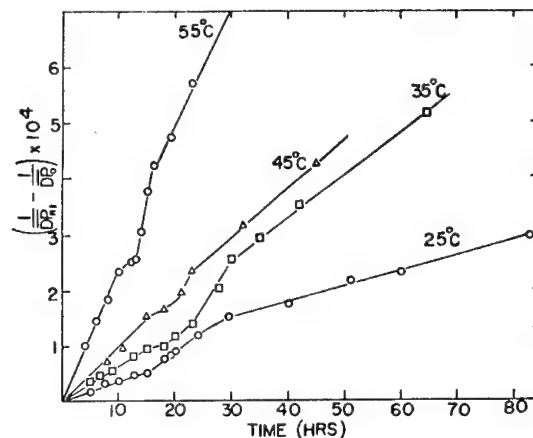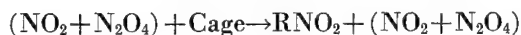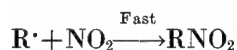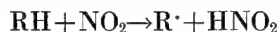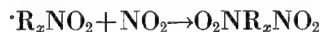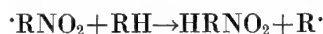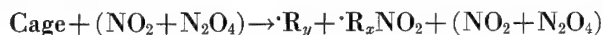

FIGURE 1. Degradation of atactic polystyrene as function of temperature (30 cm Hg of NO_2).

obtained in benzene solutions. Curves were obtained on dilution, which suggested that disaggregation of polymer molecules took place. Apparently, NO_2 and peroxide side groups are formed which make the chains polar, causing them to aggregate in benzene solution. This effect disappeared on further exposure. Straight lines, however, could be obtained for these plots in dioxane solution at all stages of the degradation process.

Degradation data can be satisfactorily accounted for by a mechanism, which can be considered to be the analog of Bolland's [5] oxidation mechanism,

$$RH + NO_2 \rightarrow R\cdot + HNO_2$$

$$R\cdot + NO_2 \xrightarrow{Fast} RNO_2$$

$$RNO_2 \rightarrow \text{Inert Products}$$

$$RNO_2 \rightarrow \langle \cdot R_x NO_2 R_j \rangle \text{ Cage}$$

$$(NO_2 + N_2O_4) + \text{Cage} \rightarrow RNO_2 + (NO_2 + N_2O_4)$$

Chain Scission:

$$\text{Cage} + (NO_2 + N_2O_4) \rightarrow \cdot R_y + \cdot R_x NO_2 + (NO_2 + N_2O_4)$$

$$\cdot RNO_2 + RH \rightarrow HRNO_2 + R\cdot$$

$$\cdot R_x NO_2 + NO_2 \rightarrow O_2 NR_x NO_2$$

$$\cdot R_y + \cdot R_x \rightleftarrows \text{Cage} \rightarrow P_y + P_x$$

RH stands for polymer, $R\cdot$ etc. for polymer radicals and P for 'dead' polymer.

Evaluation of this kinetic scheme leads to,

$$\alpha = K_m P_{\text{total}} P_{NO_2} \left[t + \frac{1}{k_8} \left(e^{-k_8 t} - 1 \right) \right] \qquad (2)$$

The final result actually contains some refinements, which will not be discussed here. A few words may be added about "cages". It is generally agreed now that chain scission and also other steps in polymerization and degradation reactions, proceed via solvent or medium cages. The problem in the case of polymerization was treated by Benson and North [6] and North [7]. A cage is considered which contains potentially two polymer radicals. The escape of these radicals from the cage is a diffusion process (we discuss here the degradation case) and can be expressed by considering its rate constant, k_3,

$$k_3 = 4\pi R_{AB}(D_A + D_B) \qquad (3)$$

R_{AB} is the maximum distance of the centers of gravity of the two imprisoned radicals in random coil configuration, at which reversal of the process to the original polymer can still occur. D_A and D_B are the respective translational diffusion coefficients of the radicals in the surrounding medium. On the average, two radicals of equal length are produced, hence, eq. (3) simplifies to,

$$k_3 = 4\pi R_{AB}(2D) \qquad (4)$$

If the Stokes-Einstein relation holds, D is given by,

$$D = \bar{k}T / \pi B' \eta \bar{R} \qquad (5)$$

$\bar{k}$ is Boltzmann's constant, B' a constant equal to six for large particles, η is the medium viscosity and $\bar{R}$ the radius of one of the radical coils. The latter is given by,

$$\bar{R}_{AB}^2 = \bar{R}_A^2 + \bar{R}_B^2 = 2\bar{R}^2 \qquad (6)$$

Introducing equations (5) and (6) into the original eq. (4) yields,

$$k_3 = \frac{8\sqrt{2}\bar{k}T}{B'\eta} \qquad (7)$$

Equation (7) is well obeyed in the case of poly-α-methylstyrene in solutions of different viscosities [8].

The diffusion constant D can be obtained from eq (5) (random coils). The root mean square radius of a polymer radical in a cage in the configuration of a random coil is given by,

$$\bar{R} = (\tfrac{1}{4}\overline{DP}_{n,t,c})^{1/2} l / (B')^{1/2} \qquad (8)$$

$\overline{DP}_{n,t,c}$ is the critical chain length where the average kinetic chain length $\bar{\epsilon}$ has just become equal to that of the polymer chains, l is the length of a structural unit of the chain, $(B' = 6)$. Calculated and experimental values for poly-α-methylstyrene in solution are quite reasonable [8].

In summary, the whole degradation process in case of polystyrene consists of a random chain scission process and incorporation of NO_2 as side groups. IR spectra for polyethylene show this incorporation quite clearly [9]. The chain scission is controlled by diffusion out of cages.
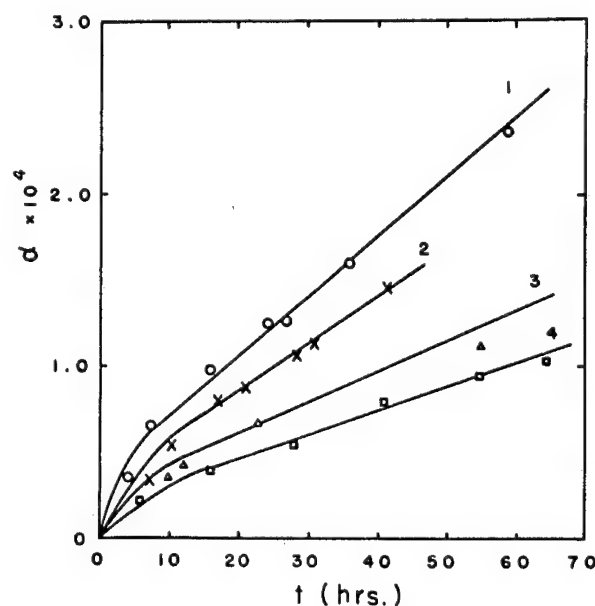

FIGURE 2. *Degree of degradation α of butyl rubber as a function of time for various NO_2 pressures in absence of air at 35 °C:*

(1) 1 mm Hg, (2) 0.5 mm Hg, (3) 0.35 mm Hg, (4) 0.20 mm Hg. The lines are calculated, the points are experimental data.
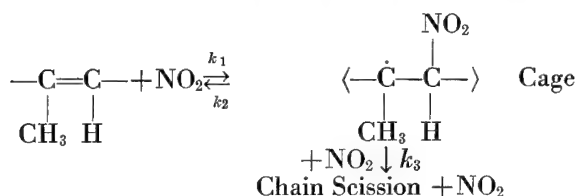
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5. Butylrubber and NO_2 [10,11]

A typical elastomer (Butylrubber) was also investigated. This polymer had an isoprene content of 1.75 percent by weight. Polymers having larger amounts of isoprene, become too sensitive for proper handling.

Here again, cast films (20–25 μm thick) were exposed under various conditions. The NO_2 pressures were quite small 0.01 to 1 mm Hg and the temperature range was 25 to 65 °C. These small NO_2-pressures were obtained in the apparatus by keeping liquid NO_2 at certain temperatures for which its vapor pressures were of the desired magnitude. Experiments were performed in absence or presence, respectively, of 1 atm of air.

Some typical degradation curves are shown in figure 2 at various NO_2 pressures (no air).

The rates of chain scission in presence of air are about five times larger than those in its absence (see fig. 3). There are a number of weak structures in butylrubber, more susceptible to chain scission than the normal ones. The chain scission reaction with NO_2 alone can be pictured as follows:

$$
-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{H}{|}}{C}-+NO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \quad \langle -\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}-\underset{\underset{H}{|}}{\overset{NO_2}{C}}- \rangle \quad \text{Cage}
$$

$$
+NO_2 \downarrow k_3
$$

$$
\text{Chain Scission} + NO_2
$$

The double bond is directly attacked by NO_2 whereas in the case of O_2 the α hydrogen atom reacts first and the unsaturation remains initially intact. Evaluation leads to,

$$
\alpha = \frac{K' P_{NO_2} t}{K + K''_{III} P_{NO_2}} = K_{exp} t \tag{9}
$$

K_{exp} is a function of the NO_2 concentration.

If O_2 is also present, three reactions take place with respect to chain scission: (1) Chain scission due to NO_2 alone, (2) Chain scission due to O_2 alone, (3) Synergistic reaction due to NO_2 and O_2.

6. Mechanism

(1) Reaction with NO_2 only:

$$
RH + NO_2 \xrightarrow{k_1} Cage_1
$$

$$
Cage_1 \xrightarrow{k_2} RH
$$

$$
Cage_1 + NO_2 \xrightarrow{k_3} \text{Chain Scission} + NO_2
$$

(2) Reaction with O_2 only:

$$
RH + O_2 \xrightarrow{k_4} R\cdot + HO_2^{\cdot}
$$

$$
R\cdot + O_2 \xrightarrow{k_5} RO_2^{\cdot}
$$

$$
\cdot RO_2 + RH \xrightarrow{k_6} ROOH + R\cdot
$$
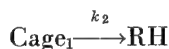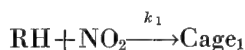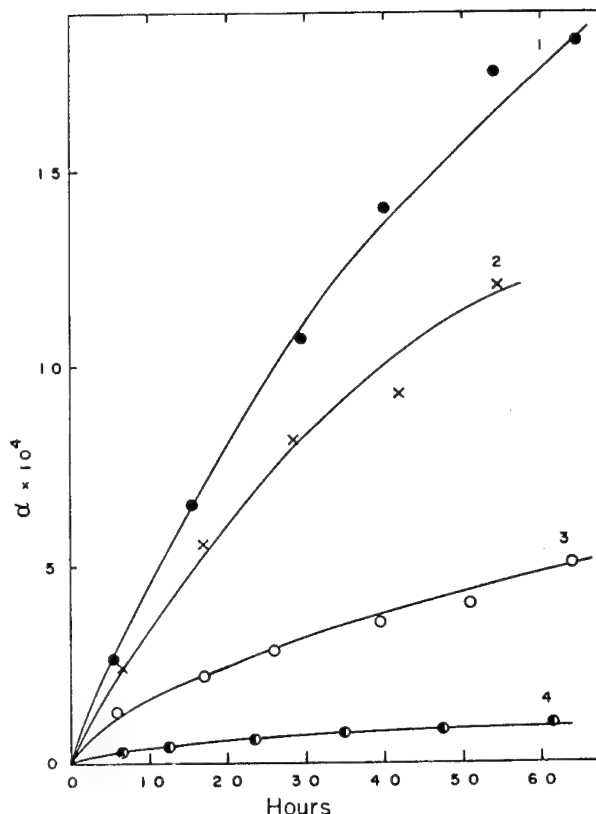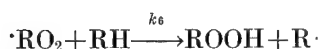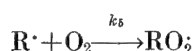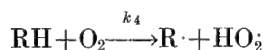
FIGURE 3. *Degree of degradation of butyl rubber in presence of 1 atm of air at 35 °C as function of NO_2 pressure and time.*

(1) 1 mm Hg, (2) 0.5 mm Hg, (3) 0.02 mm Hg, (4) 0.01 mm Hg.

$$
ROOH \xrightarrow{k_7} \text{Inert Products}
$$

$$
ROOH \xrightarrow{k_8} Cage_2
$$

$$
Cage_2 \xrightarrow{k_9} ROOH
$$

$$
Cage_2 + O_2 \xrightarrow{k_{10}} \text{Chain Scission} + O_2
$$
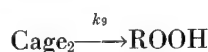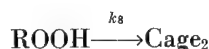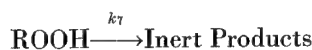
(3) Synergistic Reaction of NO_2 and O_2:

$$
ROOH + NO_2 \xrightarrow{k_{11}} NO_2 - ROOH
$$

$$
NO_2 - ROOH \xrightarrow{k_{12}} Cage_3
$$

$$
Cage_3 \xrightarrow{k_{13}} NO_2 - ROOH
$$

$$
Cage_3 \xrightarrow{k_{14}} \text{Chain Scission}
$$

$$
R\cdot + R\cdot \xrightarrow{k_{15}} Cage_4
$$

$$
Cage_4 + O_2 \xrightarrow{k_{16}} R\cdot + R\cdot + O_2
$$

$$
Cage_4 \xrightarrow{k_{17}} R - R
$$
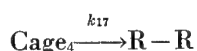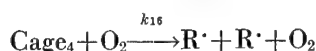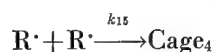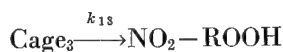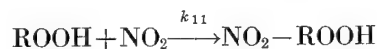
If such a mechanism is evaluated, it leads to an

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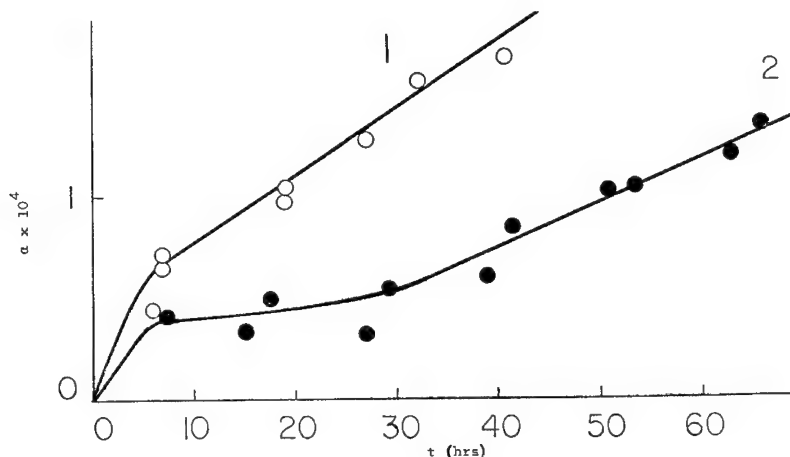
FIGURE 4. α versus t for 1 mm Hg of NO_2 at 35 °C with and without near uv irradiation (no O_2), (1) without, (2) with irradiation.

equation as follows:

$$\alpha = K_{\exp}t + \frac{K_{\exp}''}{K_{VI}^3}\left(1 - e^{-K_{VI}t}\right). \qquad (10)$$

This equation represents the experimental data well.

Studies were extended to include the effect of near u.v. light [11]. Figure 4 shows a comparison of α versus t in presence and absence of near uv radiation (1 mm Hg of NO_2, 35 °C, no O_2). Actually NO_2 retards chain scission when near uv light is present.

Figure 5 gives data for degradation in presence of uv radiation, 1 atm of air and various NO_2 pressures at 35 °C. One curve in the absence of radiation is also shown.

As pointed out above, NO_2 reacts directly with a double bond forming a radical $\sim\overset{NO_2}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\overset{|}{\underset{H}{\overset{|}{C}}}\sim$ which is located in a cage. The actual mechanism suggested is as follows,

Reaction with double bond:
negligible on exposure to
near uv radiation.

$$RH + h\nu \longrightarrow R\cdot + H\cdot$$

$$R\cdot + NO_2 \longrightarrow RNO_2 \text{ Inert Product}$$

Reaction with double bond:
$$RH + NO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \langle RHNO_2 \rangle \text{ Cage}$$

$$\langle RNO_2 \rangle + h\nu \overset{k_3}{\longrightarrow} \text{Inert Product}$$

$$\langle RNO_2 \rangle \overset{k_4}{\longrightarrow} \text{Chain Scission}$$
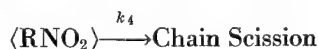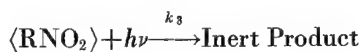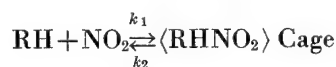
Evaluation gives,

$$\alpha_1 = \frac{k_1 k_4 [n']_0 [NO_2] t^2}{[n]_0} = K_{\exp,1}t^2 = K'_{\exp,1}[NO_2]t^2 \qquad (11)$$

$[n']_0$ and $[n]_0$ are the initial isoprene and total monomer concentration, respectively. $K_{\exp,1}$ is a function of NO_2 pressure. In absence of light the corresponding relation is $\alpha = K_{\exp,1}t$.

Photo-oxidation (no NO_2) leads to,

$$\alpha_2 = \frac{[n']_0 k_1 k_6 k_8 [O_2] t^2}{2 k_7 [n]_0} = K_{\exp,2}t^2 = K'_{\exp,2}[O_2]t^2 \qquad (12)$$

The tentative mechanism is as follows:

$$RH + h\nu \overset{k_1}{\longrightarrow} R\cdot + H\cdot$$

$$R\cdot + O_2 \overset{k_2}{\longrightarrow} RO_2\cdot$$

$$\cdot RO_2 + RH \overset{k_3}{\longrightarrow} ROOH + R\cdot$$

$$ROOH \underset{k_5}{\overset{k_4}{\rightleftarrows}} Cage_4$$

$$Cage_4 + O_2 \overset{k_6}{\longrightarrow} \text{Chain Scission} + O_2$$
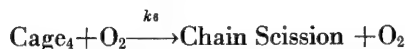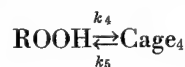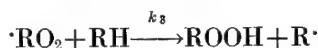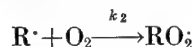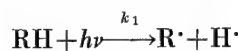
Addition of NO_2 gives $\alpha_3 = K_{\exp,3}t^2$; $K_{\exp,3}$ here is a function of O_2 and NO_2 pressure, respectively. If the NO_2 pressure is increased, the mechanism changes. The experimental curves change from convex to concave towards the time axis. An additional step seems to become significant, where NO_2 reacts directly with the double bond, which was the case when this gas is present alone: $R\cdot + NO_2 \rightarrow RNO_2$ (Inert). The degree of degradation in this case is given by,

$$\alpha = K_{\exp,3}t^2 + K_1[NO_2](1 - e^{-k_3 t}) \qquad (13)$$

For sufficiently high NO_2 pressures α reduces to the second term and for sufficiently small NO_2 pressures only the first term has to be considered.

7. Diffusion of NO_2 in Atactic Polystyrene Films [12]

A detailed study was carried out on diffusion of NO_2 through several polystyrene films. Diffusion
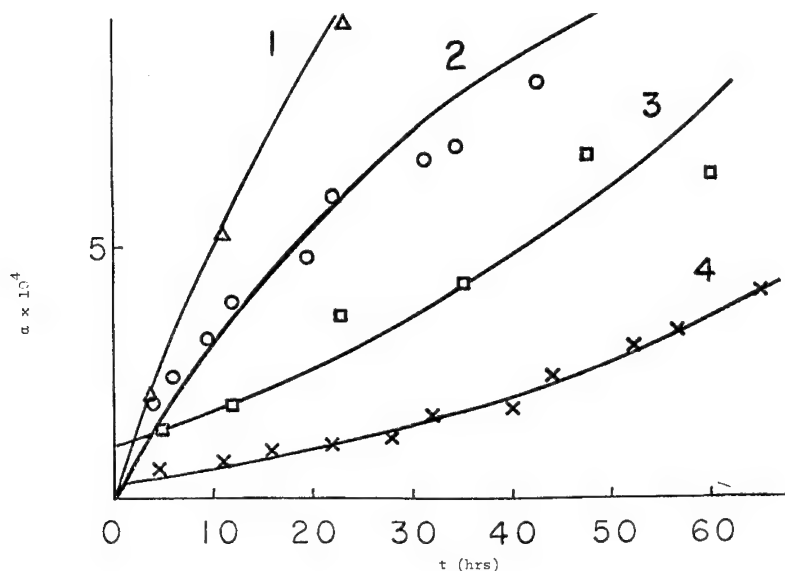
FIGURE 5. *α versus t for 1 atm air at 35 °C near uv irradiation (except curve 1) and various NO₂ pressures in mm Hg:*

(1) dark reaction, 1; (2) 1; (3) 0.5; (4) 0.2.

coefficients were determined by two different methods, whose data agree quite satisfactorily: (1) Penetration and (2) Sorption-Desorption experiments. A special device was constructed for the first method which is illustrated in figure 6. The polymer films were arranged in the form of a tightly packed deck of cards. After diffusion time, each film was analyzed and its α value was determined. (This is the first time that α was taken as a indicator of diffusion). The plot of α versus distance from the exposed film surface was used for evaluation of the diffusion coefficients. Sorption-Desorption curves are shown in figure 7. The penetration experiments were evaluated according to

$$\frac{C_{NO_2,x}}{C_{NO_2,x=0}} = \text{erfc} \frac{x}{2(D_pt)^{1/2}} \qquad (14)$$

$C_{NO_2,x}$ and $C_{NO_2,x=0}$ are the NO_2 concentrations at distances x and $x=0$ from the exposed polymer surface, D_p is the diffusion coefficient and t the diffusion time. It was found experimentally that the degradation and incorporation of NO_2 can be neglected.

The sorption-desorption experiments were evaluated by a relation as follows,

$$W_t/W_\infty = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2}$$

$$\cdot \exp\left\{-\left(\frac{(2n+1)\pi}{2a}\right) D_{S,D}t\right\} \qquad (15)$$

Here W_t is the weight sorbed or desorbed, respectively, at time t and W_∞ that at saturation. D_S and D_D are the respective diffusion coefficients for sorption or desorption, respectively, (usually the average of the two coefficients is taken). The

diffusion coefficients are of the order of 10^{-9} cm²/s. The Arrhenius energy of activation for all diffusion coefficients (Penetration and Sorption-desorption) are: $P_{total} > 10$ cm: (8.6 ± 1.8) kcal/m, and for $P_{total} = 2$ cm: (9.4 ± 5.3) kcal/m. (The $\pm$ values are standard deviations.)

8. Isotactic Polystyrene and Sulfur Dioxide [13,14]

An investigation of the effect of sulfur dioxide on isotactic polystyrene was carried out. This reaction
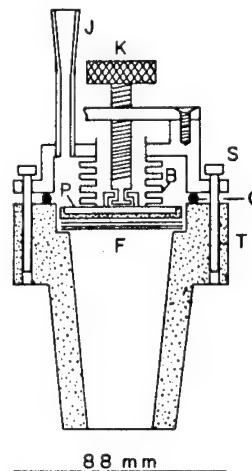
FIGURE 6. *Diffusion cell.*

B metal bellows
K screw for tightening bellows
J special connection to high vacuum at far side of films
F set of films (ca. 40 μm each)
O Viton-O-ring
T Teflon joint
P Teflon covered back plate
S screws

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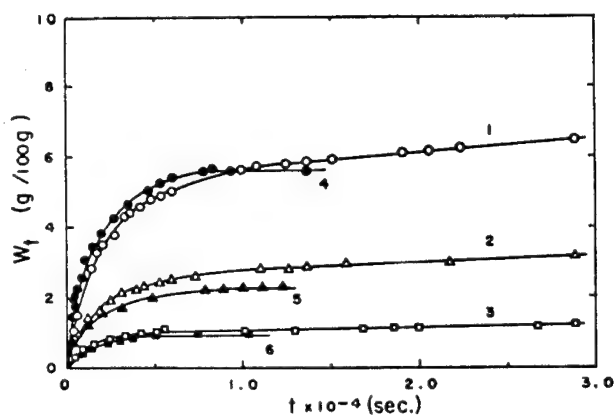
FIGURE 7. *Sorption-desorption curves of* $(NO_2 + N_2O_4)$ *for polystyrene at 45 °C.*

Sorption: (1) 60 cm, 69.1 μ; (2) 30 cm, 78.0 μ; (3) 15 cm, 78.0 μ. Desorption: (4) as (1); (5) as (2); (6) as (3).

was studied in the presence of constant light intensity, oxygen and SO_2 pressures as function of temperature (30 °C to 57 °C). Small pressures (e.g. 0.85 mm Hg) of SO_2 have quite an appreciable effect on the polymer, leading to chain scission in presence of 150 mm Hg of O_2 and near uv light. (SO_2 alone at thisn pressure has no effect). Films were cast from chloroform solutions (ca. 25 μm thick). Random chain scission takes place, which can be expressed by

$$\alpha = \frac{1}{DP_{n,t}} - \frac{1}{DP_{n,0}} = K_{exp}t \qquad (16)$$

The Arrhenius energy of activation amounts to 4.5 kcal/m, the preexponential factor is very small $(1.02\times10^{-2}\ hr^{-1})$. The light intensity exponent was found to be 1.2.

A mechanism which accounts satisfactorily for the experimental results was suggested:

$$RH+O_2 \xrightarrow{h\nu} R^{\cdot}+HO_2^{\cdot} \qquad\qquad k_1$$

$$SO_2 \xrightarrow{h\nu} SO_2^* \qquad\qquad k_1'$$

$$SO_2^* \longrightarrow SO_2 \qquad\qquad k_2'$$

$$RH+SO_2^* \longrightarrow R^{\cdot}+{\cdot}HSO_2 \qquad\qquad k_2$$

$$R^{\cdot}+O_2 \longrightarrow {\cdot}RO_2 \qquad\qquad k_3$$

$${\cdot}RO_2+RH \longrightarrow ROOH+R^{\cdot} \qquad\qquad k_4$$

$$ROOH \longrightarrow Inert\ Products \qquad\qquad k_5$$

$$ROOH+SO_2 \longrightarrow Inert\ Products \qquad\qquad k_6$$
$$(e.g.\ ROSO_2H)$$

$$ROOH+SO_2 \underset{h\nu}{\rightleftharpoons} Cage_1 \qquad\qquad k_7, k_8$$

$$Cage_1 \longrightarrow Chain\ Scission \qquad\qquad k_9$$

$$ROOH \rightleftharpoons Cage_2 \qquad\qquad k_{10}, k_{11}$$

$$Cage_2 \longrightarrow Chain\ Scission \qquad\qquad k_{12}$$

$$R^{\cdot}+SO_2 \longrightarrow {\cdot}RSO_2 \qquad\qquad k_{13}$$

$${\cdot}RSO_2+RH \longrightarrow {\cdot}R+RSO_2H \qquad\qquad k_{14}$$

$$RSO_2H \longrightarrow Inert\ Products \qquad\qquad k_{15}$$
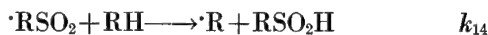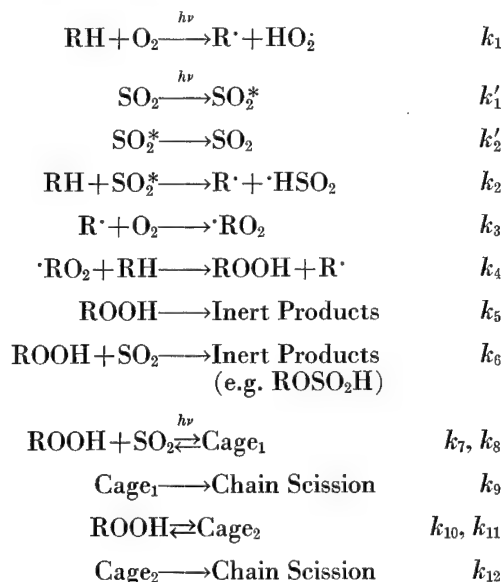
The degree of degradation α for this reaction scheme becomes

$$\alpha = \frac{\left(k_1[O_2]+\dfrac{k_1'[SO_2^*]}{k_2'+k_2[n]_0}\right)k_3[O_2]}{(k_5+k_6[SO_2])\,(k_3[O_2]+k_{13}[SO_2])}$$

$$\times \left\{\frac{k_7k_9}{k_8}[SO_2]+\frac{k_{10}k_{12}}{k_{11}}\right\}t$$

$$= K_{exp}t. \qquad (17)$$

Figure 8 gives some rate constants for isotactic polystyrene as function of SO_2 pressure (15 cm Hg of O_2) [14].

9. The Effect of Morphology on Degradation in Presence of SO_2 and NO_2, respectively [15,16]

Still more recently, work has been initiated on the effect of morphology (the percentage of crystallinity was changed) on the stability of various polymers such as isotactic polystyrene [15] and Nylon [16].

The amount and type of crystallinity depends on the mode of preparation of a particular polymer. Melting a polymer and slow cooling usually produce crystallinity. Also slow precipitation from hot solution yields crystalline polymers. The crystalline morphology is usually present in a variety of stages, sizes of crystallites and crystalline size distribution: needles, single crystals, spherulites, fibrils and so on. Orientation of polymer films and fibers also leads to crystallinity. The arrangement of individual chains in the crystallites is of great importance. Chain folding was found in this work to be of great signifi-
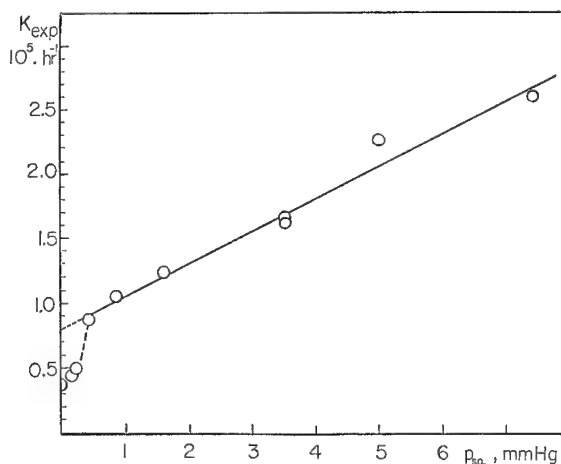
FIGURE 8. *Experimental rate constants for isotactic polystyrene as function of sulfur dioxide pressure (15 cm Hg of O_2).*

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cance for chain scission. The main chain links in the folds due to their additional energy content are more susceptible to chain scission than the links in the straight chain portions. The type of crystallites and their structure are best illustrated by some characteristic drawings (figs. 9, 10).

The polymer films prepared in this work, were characterized under a polarizing microscope and the approximate percentage crystallinity was obtained from density measurements. Isotactic polystyrene in practically amorphous form and films of various degrees of crystallinity (fibrils) were degraded in presence of 150 mm Hg of O_2, constant light intensity ($\lambda > 2800$ Å) and various SO_2 pressures over a range of temperatures. Random degradation took place. Degradation was slowest for the amorphous sample (0.93×10^{-9} s^{-1}), the crystalline films degraded at about twice this rate for 1.0 mm Hg of SO_2. At higher SO_2 pressures the discrepancy increased: 3:1 for amorphous:crystalline. The energy of activation for amorphous films is practically zero whereas for crystalline films (ca. 5 percent w/w), it amounts to 4.5 kcal/m. The increase in the experimental rate constants with w/w percentage crystallinity is shown in Fig. 11. It follows approximately a straight line. It was ascertained that the increase in these rate constants is not simply a concentration effect, by assuming that SO_2 reacts only with the amorphous polymer portion. Apparently the difference in stability is due to the many folds of the chains in the

A. FOLDED CHAIN THEORY
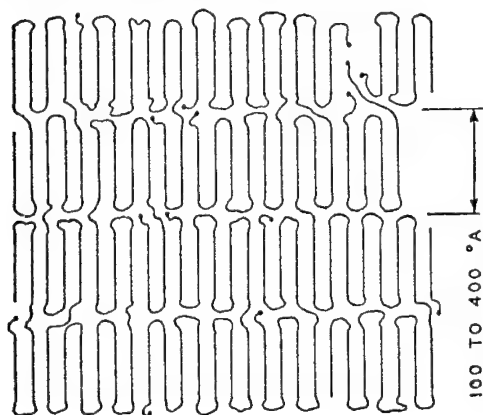
B. FRINGE-MICELLE THEORY
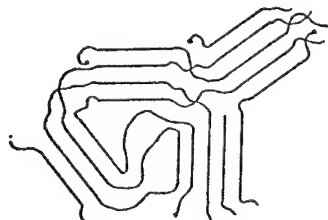
FIGURE 9. *Morphology of crystalline polymers.*

A. Schematic diagram of polymer crystallite made up of folded chains. B. Crystallites and amorphous regions according to the fringe-micelle theory.

FIGURE 10. *Crystallization from solution according to the picture of Schramm, Trillat and Sella, and Dolmetsch*

(a) Coil model. (b) After coiling, to an extent depending on chain stiffness, the molecule assumes a zig-zag form. (c) Several folded molecules aggregate end-to-end and form an elementary fibril.

crystalline polymer which have additional energy content because of strain and are better able to escape from cages. The susceptibility of main chain links in folds to degradation was also noticed in the case of reaction of nitric acid with polyethylene [17]. The reaction of O_2 is diffusion controlled under the experimental conditions; this was found in previous work on oxidative degradation of isotactic polystyrene [18]. However, SO_2 is quite soluble in isotactic polystyrene and diffusion does not play a role for this gas. Similar experiments were carried out in the presence of NO_2 [15]. This gas has an appreciably different effect; while in the case of SO_2 the rate constants increase approximately linearly with weight percentage of crystallinity, in the case of NO_2, these constants only increase initially until a relatively small percentage of crystallinity (8 percent w/w) is reached, but then remain constant with further increase in crystallinity. The explanation for this behavior is only tentative. Here again the main chain links in folds may be assumed to degrade faster than those in the straight line parts. It was pointed out that oxidative degradation is diffusion controlled; the diffusion coefficient for O_2 into polystyrene is actually larger than that for NO_2. Hence the reaction with NO_2 must also be diffusion controlled. The diffusion rates will decrease with increasing crystallinity, at the same time the rate of reaction will increase with crystallinity. There must come a point where the reaction becomes completely diffusion controlled and the rate constants from this stage on remain constant.

Some studies are now being carried out on Nylon [16] (amorphous and samples containing sperulites). The crystallinity was again characterized with the polarizing microscope and by density measurements. Exposure to NO_2 alone (0.5 mm Hg) leads to chain scission, which ceases at a definite time. The crystalline material shows about twice the rate of that of the amorphous polymer. The Arrhenius parameters for either sample are practically identical. Oxygen and uv light accelerate the reaction. The rate in this latter
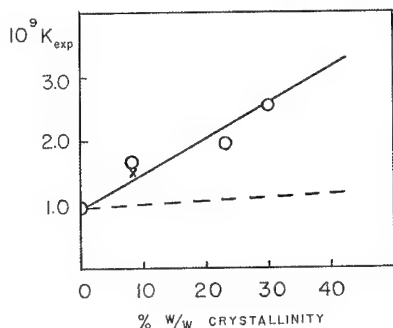
FIGURE 11. *Experimental rate constants as function of crystallinity for isotactic polystyrene as function of percentage of crystallinity.*

Dotted line: rate constants as function of SO_2 concentration in amorphous parts of films only, zero concentration in crystalline parts.

case is also faster for the crystalline material. These studies have not yet been concluded; however, it seems to be the case that a concentration effect is operative. The number of susceptible folds and hence the number of "weak" links is larger for the crystalline samples than for the practically amorphous ones.

10. Summary

Atactic, isotactic polystyrene and butyl rubber have been degraded by NO_2 gas alone near room temperature. In presence of oxygen, the chain scission rate is enhanced. In some instances NO_2 gas can actually function as retarder if near uv light is present. In contrast to oxygen, NO_2 attacks double bonds in elastomers directly. Usually, diffusion does not play a role with thin films of the order of 20 μm. Isotactic polystyrene seems to be an exception. SO_2 alone is not reactive (0.85 mm Hg). Diffusion was studied for thick films; the diffusion coefficient from penetration and sorption-desorption experiments, taking the degree of degradation as indicator for the progress of diffusion, agree well with each other. The order of magnitude of the diffusion coefficients is similar to those usually obtained for gas diffusing through polymers. Polymer morphology has appreciable influence on the stability of polymers with respect to NO_2 and SO_2 in conjunction with oxygen and near ultraviolet light. Contrary to expectations, the rate of degradation in crystalline

isotactic polystyrene (SO_2 and NO_2, respectively) and Nylon (NO_2 only) are about twice those corresponding to amorphous polymers. Indications are that main chain links in chain folds of the polymer degrade faster than links in the straight chain portions, because of excess energy in the folds.

11. References

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Discussion

Frank R. Mayo (Stanford Research Institute)

While this manuscript contains some interesting new data, some of the mechanisms presented in explanation cannot be taken very seriously. For example, reaction 16 on page 96[2] says that two caged

polymer radicals can collide with oxygen in a polymer matrix without reacting with either oxygen or each other. This reaction cannot be mechanistically significant. I know of no precedent for reaction 4, page 97; the usual cleavage occurs at the O–O bond. Reaction 9 in the same set seems most improbable; a hydrogen atom should readily abstract a hydrogen atom from the polymer before it could find a peroxy

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[2] Page numbers here refer to those in preprints.

radical. The set of reactions on page 99 neglects the reaction of R—$\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\cdot$ radicals with oxygen and ignition by $RO_2H + SO_2$.

H. H. G. Jellinek:

In answer to Dr. Mayo's remarks I should like to make the following observations. He maintains that "some of the mechanism cannot be taken very seriously." In answer to this I wish to say that in general all reaction mechanisms contain considerable elements of doubts; for example Bodenstein's mechanism for hydrogen iodide formation held up very well for about sixty years. As far as the specific comments are concerned my answers are as follows: (1) reaction 16: this reaction does not seem to be unreasonable to me as some additional energy is needed and collision with the reactive sites of the polymer radicals will be very much more unlikely than collision with the cage system as such. I agree that reaction 4 is not correct. I have omitted reactions (4), (5) and (9) in that mechanism. From a kinetic point of view they are superfluous anyway. Reaction (9) was already eliminated when finalizing the paper on this topic (ref. 11). Reaction (2) actually implies that SO_2^* is the reacting species. I have formulated this more specifically now. The reaction $R-SO_2+O_2$ does not enter into calculations which have any connection with the chain scission reaction and does not need to be considered.

W. Lincoln Hawkins (Bell Laboratories)

The reactions of isotactic polystyrene with SO_2 in the presence of oxygen may be important in the oxidation of polymers inhibited with various sulfur compounds. It has been shown that aromatic disulfides inhibit the oxidation of polyolefins, presumably by catalyzing the decomposition of hydroperoxides into inert products. In the course of the reaction of naphthyl disulfide with organic peroxides, it has been determined that traces of SO_2 are formed. The catalytic effect of SO_2 in peroxide decomposition has been demonstrated in these systems, supporting the reaction

$$ROOH \rightarrow \text{inert products} \quad k_5$$

shown in the kinetic scheme for the oxidation of isotactic polystyrene.

Controlled Gaseous Oxidations of Organic Compounds

C. F. Cullis

The City University, London, England

The homogeneous gaseous oxidation of organic compounds generally leads to a wide variety
of products and this may be ascribed not only to the occurrence of a number of consecutive and
concurrent reactions but also to the fact that the various constituent elementary steps tend to
interact with one another in complex ways. Several methods are outlined for minimising the extent
of unwanted consecutive reactions but it appears to be much more difficult to restrict undesirable
concurrent reactions. If the mutual influences of the various part-reactions are to be understood
and controlled, it is important to elucidate the nature and role of the intermediate molecular
products. Although here carefully planned experiments involving the artificial addition of reactive
intermediates can yield some information, a much fuller understanding of the quantitative im-
portance of the different competing reaction paths can be obtained from experiments with iso-
topically-labelled intermediates. Several examples are given of the use of isotopic tracer techniques
in the unravelling of the mechanism of complex gaseous oxidation reactions.

Key words: n-butane; 1-butene; 2-butene; concurrent reactions; consecutive reactions; controlled
oxidation; conventional additive experiments; cool-flames; n-heptane; intermediate products;
isobutane; isotopic tracer techniques; isotopically-labelled additives; macroscopic stages; mutual
influences; O-heterocycles; radio gas chromatographic analysis; selective inhibition; selectivity;
self-inhibition; thermal control.

1. Introduction

The oxidation of organic compounds by oxygen is
one of the most widespread of all chemical processes
used by man. Thus the combustion of hydrocarbons
in air is still among the most important sources of
heat or mechanical energy, but if this energy is to be
used to the best advantage, the chemical reactions
taking place must be suitably controlled. One of the
crudest forms of control consists in more or less
complete inhibition as exemplified by the use of
"anti-knock" additives to eliminate "knock" in
internal combustion engines. Another example of
similar rigid control is to be found in the ability of
suitable antioxidants to prevent or severely minimise
the oxidation by air of solid or liquid organic com-
pounds at or near ambient temperatures.

Nowadays the various fractions of petroleum,
which consist almost exclusively of hydrocarbons,
are being used to a rapidly increasing extent as
starting materials for the production of other
chemicals, and controlled oxidation by air or oxygen
is one of the most important reactions to which such
compounds are subjected. In this case, what is
wanted is no longer to inhibit reaction completely
but rather to exercise a more subtle and refined form
of control, so that oxidation is encouraged to proceed
selectively along a particular desired route giving
high yields of specific intermediate products.
Although such controlled oxidation of organic com-
pounds can be effected either in the gas phase or in
the liquid phase and may be assisted by both
homogeneous and heterogeneous catalysts, this

paper is concerned primarily with possible ways of
'directing', as it were, the purely gaseous processes
taking place at moderately elevated temperatures.

2. The Principal Complicating Factors

The homogeneous gaseous oxidation of organic
compounds provides an example, par excellence, of a
system involving a large number of consecutive and
concurrent stages. Now, even in the case of a very
simple chemical system consisting of, say, two
consecutive first-order reactions:

$$A \xrightarrow{k_1} B; \qquad B \xrightarrow{k_2} C$$

the kinetics are relatively complicated. Harcourt and
Esson [1],[1] over a hundred years ago, first integrated
the differential equations concerned and showed that
the concentration of the final product, C, is given as a
function of time, t, by the expression:

$$C = A_0 \left[1 + \frac{1}{k_1 - k_2} \left(k_2 e^{-k_2 t} - k_1 e^{-k_1 t} \right) \right].$$

Various possible combinations of consecutive first-
order and second order reactions were later con-
sidered in detail by Chien [2], who carried out the
difficult integrations involved. In general, however,
for reactions more complex than these "ideal" cases,
the relevant equations can be handled mathe-
matically only by making certain (often rather

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[1] Figures in brackets indicate the literature references at the end of this
paper.

drastic) simplifying assumptions. The complexity in the case of real systems involving the oxidation of even the simplest organic compounds is of course enormously greater; for not only are the various part-reactions themselves complex free radical chain processes but many of the intermediate products formed exert specific effects (the nature and magnitude of which are highly dependent on the prevailing experimental conditions) on the reactions of the other species present. Thus, in order to isolate high yields of a specific intermediate product, such as C, in a system of the type:

$$A \longrightarrow \begin{array}{c} B \\ [C] \longrightarrow D \longrightarrow E \\ F \longrightarrow G \end{array}$$
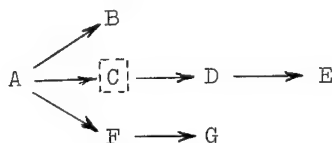
it is clearly necessary to control not only unwanted consecutive and concurrent steps but also the mutual interactions of the various reactions involved.

3. Control of Consecutive Reactions

Perhaps the most obvious way of eliminating or at least minimising the further reaction of desired intermediate products is to carry out oxidation at very low conversions. Thus, for example, Knox [3] has shown that, although the oxidation of propane leads eventually to a complex mixture of products, nevertheless if measurements are confined to the first 1–2 percent of reaction, propylene is effectively the sole organic product formed.

In other systems, including some where complications might at first sight be expected to be rather severe, Nature comes to one's aid in the sense that the very presence of certain intermediate or final products simplifies the overall behaviour. Thus in the system:

$$A \longrightarrow B \longrightarrow C$$
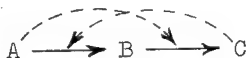
A may inhibit the conversion of B to C. One example is provided by the oxidation of primary aliphatic alcohols [4]. Here the initial product formed is the corresponding aldehyde, which would be expected, at the relatively high temperatures concerned, to undergo rapid further oxidation and in so doing perhaps act as a degenerate-branching agent leading to other modes of attack on the original alcohol. However, in practice, the alcohol present inhibits the further oxidation of the aldehyde [5], so that, at least in the earlier stages of reaction, the conversion:

$$RCH_2OH + O_2 \rightarrow RCHO + H_2O_2$$
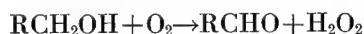
takes place more or less quantitatively.

Several examples are known too of the opposite type of behaviour in which the overlapping of consecutive reactions is limited by the inhibition by the products of initial attack of the starting com-

pound. In other words, the oxidation of the original organic compound becomes self-inhibited, so that reaction ceases while considerable amounts of both initial reactants are still present. Self-inhibition is quite frequently observed, for instance, during the oxidation of alkenes [6], amines [7], and organic sulphur compounds [8, 9]. Another example is provided by cool-flames which are, by their very nature, clearly self-inhibiting. Here the "product" responsible for the inhibition has not been unambiguously identified but there is reason to believe that this may be largely the heat of reaction [10] rather than a particular chemical species.

In other cases, it may be possible to reduce the extent of unwanted consecutive reactions by the use of additives which cause *selective inhibition* of certain stages. Very little work has been done in this field but perhaps one example may show that the subject is at least worthy of further attention. Thus tertiary amines are powerful inhibitors of the oxidation of aldehydes [11] but have little or no effect on the oxidation of ethers under similar conditions [12]. Now clearly, if an additive can be found which inhibits the further oxidation of an intermediate product without affecting its rate of formation, the isolable yields of this product will be increased.

Other additives, although not necessarily inhibiting so completely certain stages of complex reactions nevertheless minimise the effects of consecutive reactions by causing oxidation to take place in well-defined macroscopic stages. A good example is to be found in the detailed studies by Emanuel and his co-workers of the catalysis of the gaseous oxidation of hydrocarbons by hydrogen bromide. In particular, investigations were made of the reaction of equimolar mixtures of propane and oxygen containing quite large amounts (3–20 percent) of hydrogen bromide at ca. 200 °C [13]. Under these conditions, the main product is acetone, the production of which obeys a quasi-unimolecular law, viz:

$$A_t = A_\infty(1 - e^{-kt})$$

where A_t and A_∞ represent the concentrations of acetone after time, t, and at the end of the reaction respectively. This law holds with different mixtures over a wide range of conditions, although A_∞ is dependent on mixture composition. In order to explain the above relationship, it was suggested that there was rapid formation of an intermediate product, C, which was a powerful catalyst for the production of acetone but itself decomposed slowly. If the decomposition of the catalyst took place according to a first-order law and each decomposition initiated a non-branching chain leading to the production of acetone, then the observed kinetics could be accounted for.

It was indeed later shown experimentally that acetone (the product) does inhibit the formation of the catalyst which is responsible for its production. Thus, if acetone is added *in advance* in sufficient concentration, there is indeed complete inhibition; but if this compound is introduced *after* the reaction

has started, it has no effect. It is therefore clear that acetone inhibits the *formation* of the catalyst but does not affect its *decomposition.* Artificial addition of acetone at various stages of the initiating re-action—along with determinations of the final yields of acetone, A_∞ being a measure of the amount of catalyst formed—makes it possible for the kinetics of the initiating reaction to be determined on their own.

The oxidation of propane, catalysed by hydrogen bromide, is therefore a reaction which can occur in well-defined stages, and this minimises the mutual effects which consecutive reactions normally exert on one another. The occurrence of more or less discreet stages of reaction is indeed confirmed by measurements of the accompanying temperature rise which shows two maxima, well separated in time, implying two different modes of heat production.

In the same way, the HBr-catalysed oxidation of isobutane also proceeds in distinct macroscopic stages [14]. Thus at 170 °C, the first step is the conversion of the hydrocarbon to tert-butyl-hydroperoxide:

$$(CH_3)_3CH + O_2 \rightarrow (CH_3)_3COOH$$
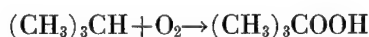
and the second step is characterised by the complete cessation of oxygen consumption and the oxidation of further isobutane solely by the hydroperoxide:

$$(CH_3)_3CH + (CH_3)_3COOH \rightarrow 2(CH_3)_3COH.$$

Again due to the (little understood) catalytic influence which the primary products evidently exert on the reactions in question, oxidation takes place in distinct stages rather than by a series of more closely interdependent steps.

4. Control of Concurrent Reactions

The effective control of unwanted concurrent reactions is in general more difficult than the corresponding problem with consecutive reactions. In order to discuss this question more fully, it is necessary to consider briefly the basic mechanism of the gaseous oxidation of organic compounds. Although it is difficult to make broad generalisations, the initial attack of the organic compound at relatively low temperatures (<400 °C) appears invariably to involve the abstraction of hydrogen to yield a free radical:

$$X + RH \rightarrow R + XH.$$
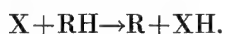
Now this step, although at first sight relatively simple, may in fact be quite complex, since the various hydrogen atoms in the organic compound will not usually all be equivalent so that a number of different radicals, R, may be formed concurrently. Thus, for example, in the gaseous oxidation of alkanes at 300–400 °C, the relative rates of attack at primary, secondary, and tertiary centres [15, 16] are, very roughly, 1:3:15. Since, however, these figures refer to relative rates per hydrogen atom, the differences in vulnerability of different parts of organic molecules may be much reduced, so that

initial attack is usually a very random process even at the lowest convenient reaction temperatures.

One possible way of increasing the selectivity of attack is to arrange that the species, X, which normally reacts with a starting compound, is replaced by some other species which attacks it with greater specificity at the most vulnerable positions. Direct studies of the reactions of atoms and free radicals with hydrocarbons have shown that the selectivity varies considerably with the nature of the attacking species and that bromine atoms are exceptionally selective in their attack, the relative rates of hydrogen abstraction from primary, secondary, and tertiary centres [17, 18] at ca. 100 °C being 1:250:6300. Since under normal conditions of gaseous oxidation, the hydrocarbon is probably attacked mainly by relatively unselective species such as hydroxyl radicals, the selectivity would be greatly increased if these were replaced by bromine atoms. This could perhaps be done by using hydrogen bromide as a catalyst when as a result of the reactions:

$$OH + HBr \rightarrow H_2O + Br$$

$$Br + RH \rightarrow R + HBr$$
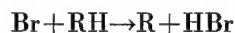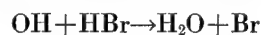
effectively only one radical, R, should be formed from an organic compound containing one preferred point of attack. Studies of the HBr-catalysed oxidation of hydrocarbons indeed tend to show rather high selectivity of product formation [19–21].

Even if the initial attack can be made to take place selectively, however, the free radicals so produced may react further in a variety of ways. On the whole it seems likely that, except at rather high temperatures, the predominant fate of R will be to react with oxygen. In this case, the first step must be the formation of some loose complex $R \ldots O_2$. This may then decompose more or less immediately to regenerate the original reactants or to give, when RH is an alkane, an alkene and an HO_2 radical. Alternatively, if the energy can be rapidly distributed between the various bonds, the complex may stabilise itself to form an RO_2 or alkylperoxy radical.

$$R + O_2 \rightleftarrows R \ldots O_2 \begin{array}{c} \nearrow \text{Alkene} + HO_2 \\ \searrow RO_2 \end{array}$$
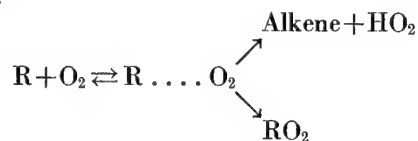
The balance between the abstractive and additive reactions will presumably not be affected by such factors as mixture composition but some control might be exerted for example by adjustment of temperature, since the activation energy is at least 10 kcal mole^{-1} (42 kjoule mole^{-1}) higher for the abstractive reaction, the use of relatively low temperatures thus favouring the additive reaction.

Even if the balance between the two concurrent reactions of the radical, R, with oxygen can be controlled, there is nevertheless a variety of possible concurrent fates which the products of these and subsequent reactions can undergo. Thus there are, to say the least, formidable difficulties in controlling

the sequence of concurrent reactions so that oxidation follows predominantly one particular route and leads to the formation of only a few specific products.

5. Control of Mutual Influences of Species Present

A number of ways have been discussed in which it may be possible to prevent or limit the occurrence of unwanted consecutive and concurrent stages during the gaseous oxidation of organic compounds and hence to exert some control on the course of the reaction as a whole. However, it is only in a very few cases that oxidation can be made to proceed solely along particular desired routes and in the majority of real systems it is necessary to investigate also the mutual influences which the various species present exert on the reactions of one another. Now, if a study is being made of the gaseous oxidation of a compound, A, this will in general lead to the formation of a number of products B_1, B_2, B_3 ...., some of which may be stable final products and others intermediate products. Certain of these intermediates may be oxidised further quite independently but some may react in such a way as to affect quite profoundly other reactions in the overall scheme. It is important, wherever possible, to discover the precise nature and role of such intermediate products, although in practice the required information is not always easy to obtain. The mere identification of a particular compound among the products of oxidation of A gives little clue as to the *role* of this compound in the reaction.

Furthermore, the failure to detect a given compound does not prove unequivocally that it is not formed or that it does not play an important part in the overall reaction. Nevertheless, there are methods for investigating the nature and role of intermediate molecular products and the information gained therefrom may be of considerable help in the unravelling of the underlying mechanism.

6. Methods of Studying Nature and Role of Intermediates

6.1. Use of Conventional Additive Experiments

One way in which it may be possible to draw useful conclusions regarding the intermediate reaction products is by means of experiments in which small amounts of possible intermediates are added to the system and their effects measured. However, experiments of this kind, unless carefully planned, are often not very informative and deductions made from them are by no means always justified. In general, significant information can be obtained only if attempts are made to seek quantitative correlations between the effect of compounds when artifically introduced into a system and the amounts of these same compounds normally formed in the system.

An example of a well-designed conventional additive experiment of this sort is provided by the work of Burgess and Laughlin [22], who studied the role of heptyl hydroperoxides during the cool-flame combustion of *n*-heptane and showed that the concentration of these compounds increased steadily prior to the passage of the cool flame but fell abruptly as the flame traversed the mixture. On the other hand, when small quantities of 2-heptyl hydroperoxide were added to the system, this compound reduced the induction period preceding the cool flame but did not affect the accompanying pressure change unless more than a certain amount was added. However the significant observation was made that the minimum concentration of peroxide required to make this occur and that normally present at the instant of passage of the cool flame were almost exactly equal; this strongly suggests that one or more heptyl hydroperoxides are the degenerate branching agents during the oxidation of *n*-heptane and that a critical concentration of these is needed to enable a cool flame to pass.

6.2. Use of Isotopically-labelled Additives

Perhaps even more significant information regarding the role of intermediates can be obtained by the use of isotopic tracer techniques and probably one of the most important and interesting cases is that where the labelled compound is an intermediate product of combustion of the fuel. Now suppose that in the system:

114
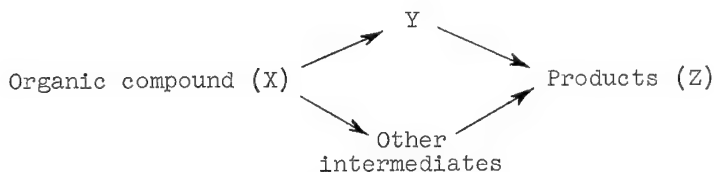
a small concentration of labelled Y is added. Measurements can then be made of the variation with time of the specific activities of Y and Z and, by quite a simple mathematical analysis, it can be shown to what extent the conversion of X to Z takes place via Y. This technique was first applied by Neiman and his co-workers and, as an illustration, mention may be made of their studies of the oxidation of methane [23], where the results show that:

100 percent of CO is formed via HCHO

25 percent of CO_2 is formed via CO.

Similarly, when propylene reacts with oxygen [24],

30 percent of CO is formed via CHO group of CH_3CHO

50 percent of CO_2 is formed via CHO group of CH_3CHO

75 percent of CH_3OH is formed via CH_3 group of CH_3CHO

<5 percent of HCHO is formed via CH_3OH.

Many of these findings are surprising and indeed show the necessity for drastic revision of previously proposed (and often widely accepted) reaction mechanisms.

Another example of the use of isotopically labelled additives in elucidating the role of intermediates in oxidation processes is concerned with the old and rather celebrated controversy regarding the extent to which the combustion of hydrocarbons (and indeed other organic compounds) proceeds via the formation of organic peroxides. One experimental finding which has tended to support the protagonists of theories which ascribe to alkyl hydroperoxides, ROOH, an important role as intermediate products during oxidation of the parent hydrocarbon, RH, is the similarity of the products of hydroperoxide decomposition to those of hydrocarbon oxidation. However, in order to establish that peroxides are true intermediates, it is necessary to show that the *mechanisms* of formation of given products are the same in the two reactions. Some studies were therefore made of the oxidation of isobutane and then, under as nearly as possible the same conditions, of the thermal decomposition of tert-butyl hydroperoxide. One product, albeit a minor one, which is formed in both reactions is methyl ethyl ketone. There are two likely routes for the production of this compound from a branched C_4 skeleton. It might be formed *either* by further reactions of acetone (which is an important product from both isobutane and tertbutyl hydroperoxide):

$$CH_3COCH_3 \xrightarrow{-H} CH_3COCH_2 \cdot \xrightarrow{+CH_3} CH_3COCH_2CH_3$$

or directly from the C_4 starting compound by some process involving migration of a methyl group, e.g.,
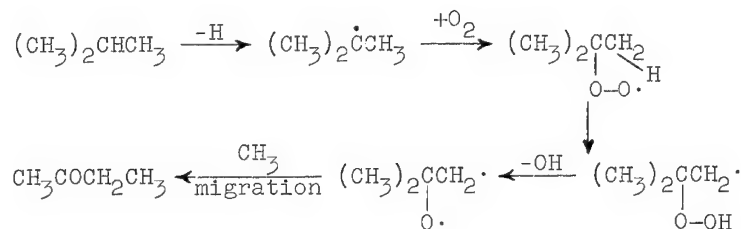
Now, if the oxidation of isobutane is carried out in the presence of ^{14}C-labelled acetone [25], the methyl ethyl ketone formed is almost completely *inactive*, i.e., it is nearly all derived from isobutane. If, on the other hand, *tert*-butyl hydroperoxide is allowed to decompose in the presence of labelled acetone [26], the greater part of the methyl ethyl ketone is *active*, i.e. it is formed via acetone. The contrast between the two mechanisms of formation of methyl ethyl ketone:

115
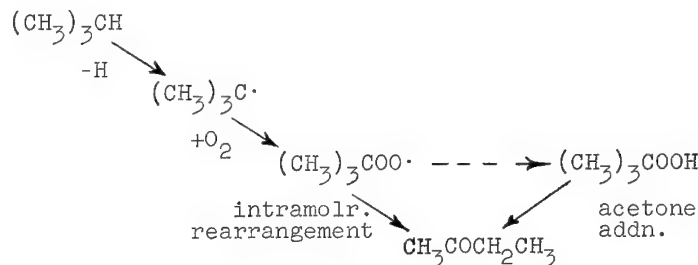
strongly suggests that the oxidation of isobutane does not, in the main, proceed via the intermediate formation of tert-butyl hydroperoxide.

Somewhat more recently, isotopically-labelled additives have been used to throw light on another point of fairly fundamental importance regarding the role of intermediates in hydrocarbon oxidation. For a time it was fairly generally agreed that, whereas at low temperatures alkyl radicals react with oxygen to give alkylperoxy radicals:

$$R + O_2 \rightarrow RO_2,$$
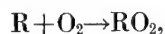
at higher temperatures this reaction leads directly to the conjugate alkene and an HO_2 radical:

$$R + O_2 \rightarrow alkene + HO_2.$$

It has lately been proposed, however, that during the oxidation of most alkanes, even at temperatures as low as 300 °C, the second reaction represents the major fate of alkyl radicals and that many, if not most, of the oxygenated products arise by the further oxidation of the intermediately-formed alkenes [27]. Experiments involving the addition of small quantities of ^{14}C-labelled 1-butene and 2-butene during the combustion of n-butane [28] make it possible to assess quantitatively the role of these compounds as intermediates. By radio gas chromatographic analysis of the products formed, i.e. by determination of both the amounts of the various products and the activity associated with them, it is possible to discover the extent to which the oxidation of n-butane proceeds via 1-butene and 2-butene and also which and how much of the various oxygenated

products arise from further reactions of the two C_4 alkenes.

The general conclusion is that, during the oxidation of n-butane at about 320 °C, the butenes play an important but not overwhelming role. The results show, for example, that at a point when the reaction rate is beginning to decrease, at least 35 percent of the n-butane has been oxidised to butenes and about 60 percent of the butenes has reacted further, 2-butene being in general a more important intermediate than 1-butene. However, that many products are being formed by a mechanism not involving butenes is shown by radio gas chromatographic analysis of the O-heterocyclic products formed. The C_4 epoxides could plausibly be formed by further oxidation of the alkenes (as in epoxidation by other reagents such as peroxyacids) but it is more difficult to see how larger ring compounds could be formed in this way and it seems more likely that these other O-heterocycles are produced by some process involving intramolecular rearrangement of the alkylperoxy radicals. The results with isotopically-labelled additives confirm these expectations. Thus, during the oxidation of n-butane in the presence of labelled 1-butene, the corresponding epoxide is radioactive, its activity indicating that between one third and one half of it arises by further oxidation of 1-butene. On the other hand, the larger ring compounds are completely inactive, showing that 1-butylperoxy radicals can be formed only by direct addition of oxygen to 1-butyl radicals and are not produced at all by the 1-butene route:
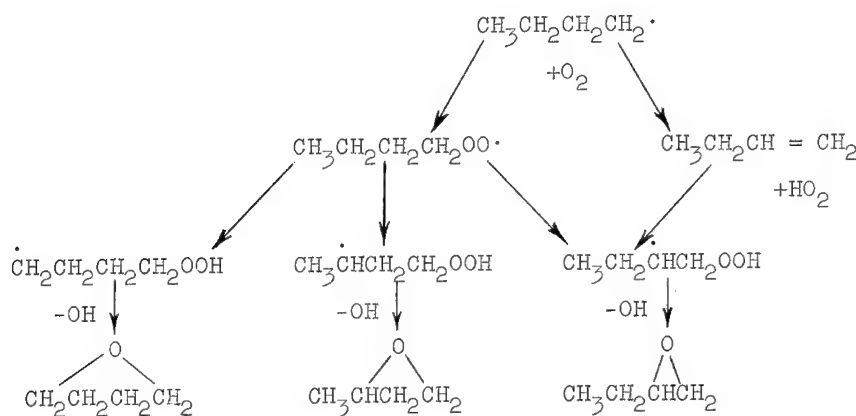
The use as additives of isotopically-labelled intermediates has also other advantages. For example, experiments of this kind can yield values for the separate rates of formation and destruction of intermediates during complex oxidation processes [29, 30]. Conventional analytical data of course provide information only about the *net* rates of accumulation of such compounds.

7. Other Forms of Control

Apart from chemical control, other types of control are clearly needed if gaseous oxidation reactions are to be successfully 'tamed' to give high yields of desired intermediate products. Thus the interaction of organic compounds with oxygen is nearly always an exothermic process, so that the efficient removal of the heat of reaction may sometimes be an im-

portant factor governing the amounts of intermediates which can be isolated. In some cases, a large temperature rise may be prevented and the yields of certain partial products increased if a 'rain' of supposedly inert solid particles is allowed to fall through the system [31]. However, solid surfaces constitute perhaps the most enigmatic of the many factors which govern the course of gaseous oxidation reactions and there seems little doubt that in most systems the surface of the containing vessel plays an important part, perhaps causing both initiation and termination of chains. Indeed, in certain circumstances, many of the characteristic reaction products formed are believed to result from heterogeneous processes [32], so that the above method of exercising thermal control may well have some influence also on the underlying chemical mechanism.

8. Conclusions

Whatever the nature of the reactants and of the desired products and whatever the type of system in which the required conversion is to be carried out, effective control cannot in general be achieved unless the reaction mechanism is fully understood. There remains therefore a pressing need for further elucidation of the processes involved during the gaseous oxidation of many organic compounds. Without a knowledge of the identity of the intermediate molecular and free radical species taking part, of the kinetic parameters of their reactions, and of the extents to which various possible consecutive and concurrent stages operate and influence one another, it is difficult to devise means of encouraging certain stages and suppressing others. It is only in this way that further useful developments may be expected which will make it possible to obtain high yields of specific intermediates instead of the complexity of products which normally results from the uncontrolled gaseous oxidation of organic compounds.

9. References

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Discussion

Alvin S. Gordon (Naval Weapons Center, China Lake, Calif.):

The use of isotopically labelled compounds to detect reaction mechanisms has been exploited very successfully by Dr. Cullis. One mechanism he has put forth states that methyl groups migrate during the course of the homogeneous gas phase reaction. Although some of the evidence presented in defense of the mechanism is quite persuasive, I find it very difficult to conceive of methyl (or alkyl) radicals migrating without the intermediary of free radicals. This is because hydrogen atoms form a very protective shield around a C–C bond, preventing a free radical from being able to react with the orbitals of the C–C bond. As an example, even H atoms cannot attack the C–C bond of a saturated hydrocarbon to form a smaller hydrocarbon and a free radical, even though the process is quite exothermic.

C. F. Cullis:

I agree with Dr. Gordon that care must be exercised when drawing detailed mechanistic deductions from the results of experiments involving isotopically-labelled compounds. However, in some studies of the gaseous oxidation of relatively large hydrocarbon molecules, the only plausible conclusion appears to be that alkyl groups do migrate, even though this may involve the intermediate formation of free radicals. Perhaps I might mention two examples taken from our earlier work.

The first concerns the slow combustion of specifically-labelled 2-methylpentanes (Cullis, Hardy and Turner, Proc. Roy. Soc. A.251: 265 (1959)). When the 4- and 5-positions are labelled with carbon-14, the labelled atom does not appear in the resulting methyl ethyl ketone whereas, when the 2- and 3-positions are labelled, the specific activities of this product are the same as those of the original labelled hydrocarbons. Both the 2- and 3-carbon atoms (but not the 4- and 5-carbon atoms) are therefore always involved in the formation of methyl ethyl ketone and, since degradation experiments show conclusively that the carbon atom in the 2-position forms the carbonyl group of the ketone, the 3-carbon atom must form the adjacent methylene group:

$$
\begin{array}{c}
1' \\
CH_3 \\
|
\end{array}
$$

$$
\underset{1\ \ 2\ \ 3\ \ 4\ \ 5}{CH_3CHCH_2CH_2CH_3} \rightarrow \underset{1\ \ 2\ \ 3\ \ 4}{CH_3COCH_2CH_3}
$$
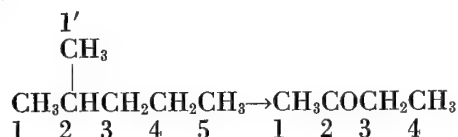
It seems highly unlikely that both of the two attached methyl groups should become separated from the tertiary carbon atom, so that the 1-carbon atom becomes the α-methyl group in the ketone. There is no direct evidence from the labelling experiments that the 1'-carbon atom becomes the β-methyl group

in methyl ethyl ketone but the fact remains that the 1'-carbon atom is split off and somehow or other a methyl group becomes attached to the methylene group which was originally in the 3-position.

A second example is provided by the formation of *tert*-butyl alcohol during the slow combustion of 2-methyl-but-2-ene (Cullis, Fish and Turner, Proc. Roy. Soc. A.267, 433 (1962)). When the 2-position is labelled with carbon-14, this appears as the α-carbon atom in the alcohol whereas, when the 4-position is labelled, the methyl groups in the resulting *tert*-butyl alcohol have some activity. The second finding makes it difficult to avoid the conclusion that the 4-carbon atom migrates so that it becomes directly attached to the 2-position:
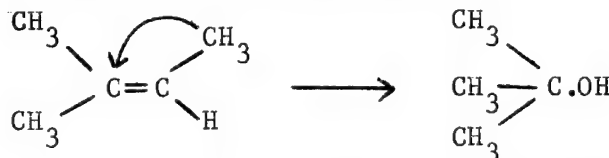
although the precise mechanism of this migration remains a matter for conjecture.

More recently evidence has been obtained that ethyl groups can migrate during the gaseous oxidation of 3-ethylpentane (Barat, Cullis and Pollard, Thirteenth Symposium on Combustion, p. 179. Pittsburgh, The Combustion Institute, 1971) but this work did not involve the use of isotopic tracer techniques.

A. S. Gordon (Naval Weapons Center, China Lake, Calif.):

As a speculation of an alternative mechanism to that proposed by Cullis, Hardy, and Turner (Proc. Roy. Soc., (1959)), for the oxidation of 2-methyl protane to acetone, I would like Dr. Cullis' comments on
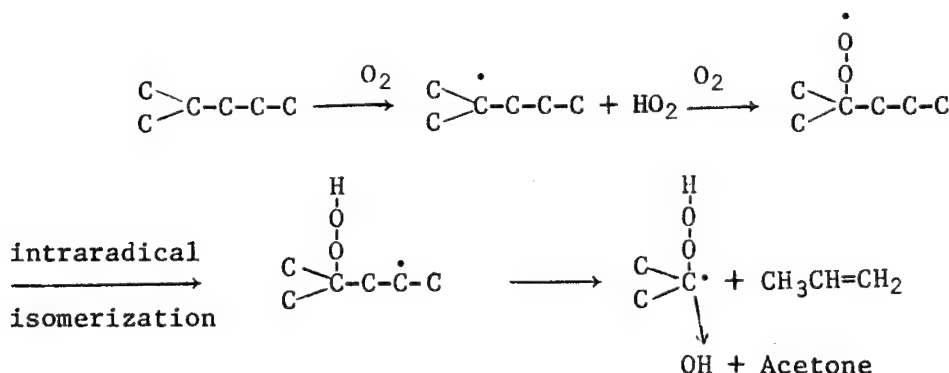
The mechanism postulates a six-membered ring for internal abstraction, which should be fairly strain free. All the energetics would be favorable. By

analogy, starting with the $\overset{\displaystyle C}{\underset{\displaystyle C}{C-\dot{C}-C-C}}$ radical, one

would form ethylene and isobutyraldehyde, an isomer of methyl ethyl ketone. Would the analyses used by Cullis et al. be able to discriminate methyl ethyl ketone and isobutyraldehyde?

C. F. Cullis:

The components of the reaction mixture were identified by carrying out gas-chromatographic analysis not only on different columns and at different column temperatures but also after artificial addition of each of the components believed to be present. In addition the combined products of several identical runs were passed through a large preparative chromatographic column; the effluent fractions were bubbled through Brady's solution and the presence of individual carbonyl compounds was confirmed from the melting points of the precipitated 2:4-dinitrophenylhydrazones.

However, although there is no doubt whatever about the presence of methyl ethyl ketone in the products, one would not want to be too dogmatic about the absence of isobutyraldehyde. At the time when the experiments referred to were carried out, gas-chromatographic columns were not nearly as well developed as they are now, when it is a very easy matter to distinguish between two compounds such as methyl ethyl ketone and isobutyraldehyde.

Questions from Audience:

Professor Cullis, please explain what you mean on the last page of your paper by using a "rain" of solids to control the temperature in an oxidation reaction.

C. F. Cullis:

I understand that Professor Jones is in the audience and if so perhaps he would like to give the explanation. Professors Jones and Fenske at the Pennsylvania State University first reported on this technique.

J. H. Jones (Pennsylvania State University):

Thank you, Dr. Cullis, for allowing me to have this pleasant task. The reaction vessel we use at Penn State consists simply of a 26-inch length of steel pipe $1\frac{1}{2}$ inches in diameter supported in a vertical position. Vapors of hydrocarbon or of any organic compound are fed into the pipe bottom and pass upwardly where they meet oxygen which is added at as many as five separate points along the length of the reaction vessel. The oxygen added at each inlet is completely consumed before the next inlet is reached. If no means were available to remove the reaction heat, the mixture of hydrocarbon and oxygen would catch on fire. Heat is removed, however, and good temperature control is achieved by allowing fine (300 to 800 μm in size) inert solids to fall through the reaction zone. The amount of solids required to remove the heat is small and occupy less than 0.5 percent of the total reactor volume. Thus, the oxidation is permitted to occur in what is essentially an open tube. In fact, for the case of C_5 to C_{16} hydrocarbons the results are identical to those obtained when using an open tube and 90 percent of an inert diluent. (The large excess of inert diluent is required in an open tube reactor in order to maintain the reaction temperature within reasonable control.)

As noted above, the amount of solids needed for good temperature control is small and has no noticeable effect on the oxidation products. However, if the amount of solids introduced is appreciably increased, then oxygenated compounds including undesirable carbon oxides are favored and finally, when an even larger excess of solids is used, the oxidation reaction can be completely inhibited.

In an early version of our reactor fitted with a window for observation, it was noted that five separate cool flames (one above each oxygen inlet) were present, each of which was at the uniform reactor temperature. Thus, such a reactor is useful in preventing the temperature from rising into the higher range where a negative temperature effect is observed.

The usefulness of the "rain" of solids for temperature control also works for chlorination reactions; thus, methane can be converted directly to carbon tetrachloride in one pass through the reactor. If solids are not employed, then such a mixture catches fire.

Some Current Problems in Oxidation Kinetics*

Sidney W. Benson, Chairman

Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, Calif. 94025

Experimental data on low temperature (<150 °C) and high temperature (>250 °C) oxidations are examined from the point of view of reported quantitative inconsistencies. Activation energies for $tBuO_2$ metathesis reactions with alkanes appear to be 7 kcal/mole higher than for comparable reactions of HO_2. Related isomerization reactions are examined in the light of these differences without reaching any simple conclusions. The Russell mechanism for a 6-membered, cyclic, transition state for termination of primary and secondary alkyl peroxy radicals is shown to be either inconsistent with thermochemical data, or else unique to solution reactions. Addition reactions of O_3 with olefins and acetylenes are shown thermochemically to have the possibility of following concerted and biradical pathways, respectively.

Recent data showing strong inhibition by PbO-coated surfaces of both oxidation and pyrolysis of $i-C_4H_{10}$ are examined in terms of mechanism.

Key words: Acetylene reaction with O_3; activation energy for oxidation; O_3 addition to unsaturates; chain lengths in oxidation; elementary steps in oxidation; epoxidation; gas-phase oxidation; kinetics; liquid-phase oxidation; mechanism; oxetane formation in oxidation; oxidation; peroxy radicals; radical isomerization; surface effects in oxidation; termination rates; transition state for termination.

1. Introduction

In 1967 an International Symposium on Combustion, held in San Francisco [1][1] seemed to offer for the first time a consistent qualitative chemical scheme tying together high and low temperature oxidation of organic molecules, and also cool flame phenomena. At that time, however, some quantitative objections were raised to the simple scheme. It is my purpose in the present manuscript to review these objections, and also the relevant kinetic data, which has been assembled since then, and to assess the current situation on oxidation mechanisms.

To facilitate the discussion, let us summarize briefly the simple aspects of the oxidation mechanism. At temperatures below 150 °C, the oxidation of most organic molecules will not proceed measurably in the absence of either catalysts or a radical initiation source. With such initiation, the major, and in some cases quantitative, product of the reaction is the hydroperoxide. The reaction can be represented by the exothermic equation:

$$RH + O_2 \rightarrow RO_2H + \sim 20 \text{ kcal} \qquad (1)$$
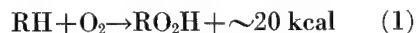
with a propagation mechanism:

$$R \cdot + O_2 \underset{-1}{\overset{1}{\rightleftarrows}} RO_2$$

$$RO_2 + RH \text{ (or } SH) \underset{-2}{\overset{2}{\rightleftarrows}} RO_2H + R \cdot \text{ (or } S \cdot) \qquad (2)$$
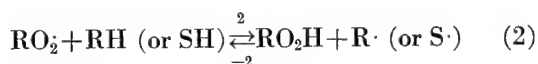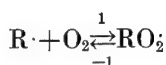
Reaction 1 in this sequence can be looked upon as a radical recombination with no activation energy. Below 200 °C, for most radicals, $R \cdot$, it is essentially irreversible [2, 3]. Its absolute rate has been measured in the gas phase for CH_3 and C_2H_5 radicals and it occurs at about 1 in 100 collisions. In solution, it is a diffusion-controlled rate constant with k (solution) $\sim 10^9$ 1/mole-s.

Between 200 and 300 °C, hydrocarbon oxidations, in the absence of initiators, show peculiar induction periods, surface sensitivity, and auto-catalysis. These phenomena, while occupying much attention, have tended to obscure the quantitative study of oxidation in this temperature range. They have demonstrated that in the course of oxidation, products are accumulated which accelerate the rate of oxidation. It is most likely that the essential auto-catalytic product is RO_2H. The half-life for its homolytic fission, $RO_2H \rightarrow RO \cdot + HO \cdot$ is about 500 seconds at 250 °C and about 2 seconds at 330 °C. RO_2H provides the "degenerate, secondary, chain-branching agent" postulated by Semenov, to account for the "cool flame" phenomena observed between 250 and 320 °C. It is by now well documented that these are real flames and by no means cool. Temperature rises of between 100 and 200 °C have been observed during cool flames. The con-

tribution of hydroperoxides to branching is obscured by the added contribution of their breakdown products, aldehydes. These latter can increase oxidation rates by providing much faster H-atom donors than alkanes in the slow propagation step 2. They can also contribute to faster initiation, but this must be a heterogeneous process below 300 °C and negligibly slow as a homogeneous reaction compared to RO_2H fission. It should not be overlooked that the end point of aldehyde supported propagation (step 2) is a hydroperoxide! The relevant mechanism can be illustrated in the case of C_2H_5OOH

$$C_2H_5OOH \overset{i}{\rightarrow} C_2H_5O \cdot + \cdot OH$$

$$C_2H_5O \cdot + O_2 \overset{1'}{\rightarrow} CH_3CHO + HO_2$$

$$C_2H_5O \cdot \overset{2}{\rightarrow} CH_2O + \cdot CH_3 \sim \rightarrow CH_3OOH \quad (3)$$
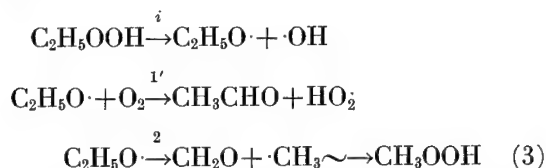
What has been astonishing about the cool flame regime and the related phenomena of multiple-stage ingition (i.e., real flame) which may accompany cool flames is the fact that cool flames are self-quenching. The equivalent phenomenon observed in flow systems is the negative temperature coefficient for hydrocarbon oxidation. Above 320 °C oxidation rates in hydrocarbon-oxygen mixtures decrease with rising temperature. The decrease in rate between 300 and 400 °C can be as much as a factor of 20. Very similar mechanisms for this negative temperature coefficient have been proposed independently by Knox [2] and the author [3] in terms of the increasing reversibility of reaction 1 (eq. 2) above 250 °C and a competing reaction leading to more stable products:

$$R \cdot + O_2 \overset{1'}{\rightleftarrows} olefin + HO_2$$

$$HO_2 + RH \overset{2'}{\rightleftarrows} H_2O_2 + R \cdot \quad (4)$$
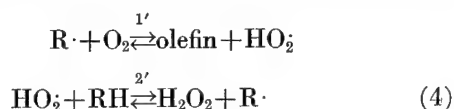
In contrast to the unstable RO_2H, the product of the high temperature reaction, HO_2H, is stable up to 450 °C and doesn't serve as a new radical initiation source much below 450 °C.

Although the negative temperature coefficient of oxidation reaction has been attributed to the decreasing production of RO_2H with increased temperatures [4], it is also true that the concomitant turnover in the nature of the propagating radical from RO_2 to HO_2 leads to an enormous increase in termination rate. Where RO_2 termination rate constants are supposed to be in the range of 10^3 to 10^6 l/mole-sec in gas phase reactions ($2tBuO_2$ can't terminate at all), termination of HO_2 with either RO_2 or another HO_2 by simple disproportionation is expected to have $k_t \sim 10^9$ l/mole-sec.

One final point should be commented upon, namely the heterogeneity or sensitivity of the oxidation rates to surfaces. I believe that primary, spontaneous initiation is a heterogeneous process in almost all systems. On the other hand, above 250 °C most radical reactions, such as fission of $RO_2 \rightarrow R \cdot + O_2$ epoxidation of hydroperoxy alkyl radicals and some

metathesis reactions of HO_2 or RO_2 (with $E_a \leq 16$ kcal), can be shown to be too fast for diffusion to the surface to be competitive above a total pressure of 100 torr.

2. The Activation Energy for Chain Propogation

There are no direct measurements of the absolute rate constants or Arrhenius parameters for the metathesis reaction of HO_2 of RO_2 radicals with alkanes. Two types of indirect study have yielded approximate values for these important reactions. One is the low temperature (50 to 150 °C) oxidation of hydrocarbons, while the other is the high temperature (440 °C) co-oxidation of CH_2O with alkanes. The latter yields values for rate of metathesis reactions of HO_2 with alkanes, rather than for RO_2, but the two radicals are expected to show similar behavior. Unfortunately, the results show considerable disagreement.

One of the most careful quantitative studies of low temperature hydrocarbon oxidation has been the work of Allara et al. [5] on both the liquid and gas phase oxidation of i-butane. They used ABN or DTBP as initiators and obtained reasonably good mass balances on O_2 consumption (90 to 97 percent).

Based on a single propagation step, $t\text{-}BuO_2 + t\text{-}BuH \overset{p}{\rightarrow}$ $t\text{-}BuO_2 + t\text{-}Bu \cdot$ and a single termination, $2t\text{-}BuO_2 \overset{t}{\rightarrow}$ $(t\text{-}BuO)_2 + O_2$, they estimated from the temperature coefficient of the rate, that $E_p - \frac{1}{2}E_t = 11.3 \pm 1$ kcal/mole. E_t had been reported earlier in the range 7.6 to 10 kcal/mole, so that the combination gives $E_p = 16 \pm 2$ kcal/mole, an unexpectedly high value for a nearly thermoneutral reaction (ΔH_p is ~ 2 kcal).

This value is consistent with $k_t \sim 10^3$ l/mole-sec, which has been reported for sector methods in C_6H_6 solution [6]. On the other hand, if $k_t = 10^7$ l/mole-sec due to contributions from other radicals, then $E_p = 12 \pm 1$ kcal/mole. If we assign $A_p = 10^{7.5}$ l/mole-sec and use the reported values at 50 °C in the pure liquid of $k_p/k_t^{1/2}$ and $k_t^{1/2}$, then we find $E_p = 14.0$ kcal/mole. Because of difficulties with the concentration dependence varying from $(RH)^{1.0}$ to $(RH)^{1.5}$ with decreasing (RH), it is not certain how much confidence to place in these values.

In a completely different type of study, Baldwin et al. [7] have studied the high temperature (400 to 550 °C) oxidation of aldehydes in aged, boric acid-coated pyrex vessels. For CH_2O, the mechanism is:

$$CH_2O + O_2 \overset{i}{\rightarrow} \dot{C}HO + HO_2$$

$$\dot{C}HO + O_2 \overset{1'}{\rightarrow} CO + HO_2$$

$$\dot{C}HO + O_2 \overset{1}{\rightleftarrows} HCO(O_2) \quad (K_{eq} \sim 10 \text{ atm}^{-1})$$

$$HO_2 + CH_2O \overset{p}{\rightarrow} H_2O_2 + H\dot{C}O$$

$$2HO_2 \xrightarrow{t} H_2O_2 + O_2$$

$$H_2O_2 + M \xrightarrow{i'} 2\dot{O}H + M$$

$$HO\cdot + CH_2O \xrightarrow{p'} HOH + H\dot{C}O$$

$$HCO(O_2^{\cdot}) + CH_2O \xrightarrow{p''} HCO_3H + H\dot{C}O \qquad (5)$$
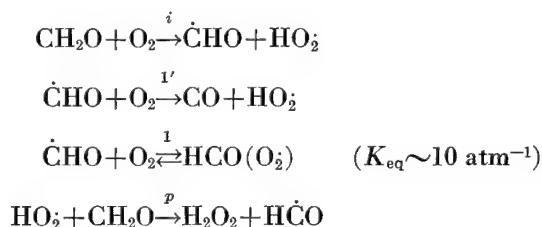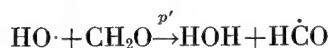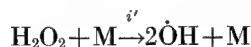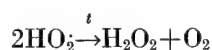
Similar studies lead to values for $k_i \sim 10^{9-45/\theta}$ l/mole-sec for the more complex C_2H_5CHO oxidation ($\theta = 2.303\ RT$ in kcal/mole). The uncertainty in Arrhenius parameters was reported as 45 ± 5 kcal/mole where the ΔH for the reaction is 40 ± 2 kcal/mole. For $k_p(EtCHO)/k_t^{1/2}$ they report a value of 43 $(1/\text{mole-sec})^{1/2}$ at 440 °C and $k_p(EtCHO) \sim 10^{9-10/\theta}$ l/mole-sec. This leads to $k_t = 10^{8.6}$ l/mole-sec. Use of the more widely quoted value of $k_t = 10^{9.2}$, the value $k_p/k_t^{1/2} = 43$ and an assigned A-factor of $10^{8.5}$ l/mole-sec yields $E_p(EtCHO + HO_2) = 7.5$ kcal/mole. This latter reaction is exothermic by 3 kcal.

When they introduce small amounts of alkanes into the $CH_2O + $ air mixture, they can follow the disappearance of alkane relative to CH_2O, presumably by reactions with the HO_2 radical. This leads to metathesis rates of HO_2 with C_2H_6, C_3H_8 and i-C_4H_{10} relative to CH_2O at 440 °C of 0.028, 0.088, 0.155. This is an astonishingly high selectivity and rules out the possibility that the propagating radical for these species is an active (hence less selective) radical, such as OH or O.

If we assume that the absolute rate of $HO_2 + CH_2O$ is twice that of $HO_2 + C_2H_5CHO$, or $10^{6.2}$ l/mole-sec, then at 440 °C the absolute rate constants for $HO_2 + $ the above alkanes are, respectively, $10^{4.6}$, $10^{5.2}$, and $10^{5.4}$ l/mole-sec. If we estimate from these rates the primary, secondary, and tertiary H-atom abstraction contributions by additivity, and assign reasonable A-factors, we can estimate the following rate parameters for HO_2 abstraction:

(primary H only) $\qquad k_p(C_2H_6) = 10^{8.5-12.7/\theta}$

(secondary H only) $\qquad k_p(C_3H_8) = 10^{8.0-9.8/\theta}$

(tertiary H only) $\qquad k_p(i\text{-}C_4H_{10}) = 10^{7.5-7.5/\theta}$
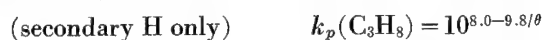
It is hard to estimate the uncertainty in the above activation energies, but they are probably not in excess of $+3$ to -1.5 kcal/mole.

E_p for the metathesis of HO_2 with i-C_4H_{10} from these gas-phase high temperature studies is thus 7.5 kcal/mole with a possible upper limit of 10.5 kcal/mole. This is in contrast with the solution values for t-$BuO_2 + i$-C_4H_{10} at 50 °C for which E_p is estimated to lie in the range 12 to 16 kcal/mole.

We can only conclude that either additional steric strain in the transition states, or solvation effects, or experimental errors, or errors in interpretation of the mechanisms are the source of these differences. At the moment we are inclined to favor somewhat increased gas-phase parameters and assume that adventitious terminations are complicating the solution results. A value of $E_p(HO_2 + i\text{-}C_4H_{10}) = 10$

kcal/mole might not be an unreasonable compromise of both with a slightly higher value by 1 or 2 kcal for t-$BuO_2 + i$-C_4H_{10}.

3. Chain Lengths in the High Temperature Oxidation

In examining the proposed high temperature mechanism propagated by HO_2, Knox [2] noted that the observed, maximum rates of reaction put some severe requirements on the propagation rate constant. Thus, R_p, the rate of reaction if HO_2 is the propagating radical, is given by:

$$R_p = k_p(RH)(HO_2)$$

subject to the termination step:

$$R_t = 2k_t(HO_2)^2$$

The kinetic chain length, λ, is given by R_p/R_t, or:

$$\lambda = \frac{R_p}{R_t} = \frac{k_p}{2k_t}\frac{(RH)}{(HO_2)} = \frac{k_p^2(RH)}{2k_t[R_p/(RH)]}$$

At 600 °K, typical values of $R_p/(RH)$ at the maximum in the rate curve are about 10^{-3} s^{-1}. If in the case of C_2H_6 we set $k_p = 10^{8.5-E/\theta}$ l/mole-s, and $k_t = 10^{9.2}$ l/mole-s, then $(HO_2)_{max} = 10^{-3}/k_p = 10^{-11.5+E/\theta}$, and

$$\lambda_{max} = k_p^2(RH) \times 10^3/2k_t$$

If we use $k_t = 10^{9.2}$ l/mole-s as suggested by Baldwin, et al. [7], we find (at (RH) ~ 100 torr) that in order for $\lambda > 1$, $E_p \leq 11$ kcal/mole. This suggests that in the C_2H_6 oxidation, either the rates suggested by Baldwin's work have too high Arrhenius parameters, or $\lambda < 1$, or HO_2 is not the main propagating radical. For C_3H_8 or i-C_4H_{10}, there is no problem. The rate constants for HO_2 metathesis listed are in agreement with the assumption that $\lambda > 1$.

A reasonable solution to this problem is that in the case of C_2H_6 oxidation, the HO_2 radical makes only a minor contribution to the overall rate (e.g., ~ 20 percent) and that a less selective radical, such as OH, does indeed do the main propagation. We could still, under these circumstances, observe H_2O_2 as a major product if nearly every C_2H_5 radical produced reacted with O_2 to form $HO_2 + C_2H_4$ and the HO_2 produced H_2O_2 either by disproportionation with itself or by abstraction from C_2H_6 or one of the more reactive aldehyde side products. These latter can be produced by reactions such as:

$$\cdot C_2H_5 + O_2 \rightleftarrows C_2H_5O_2^{\cdot}$$

$$2C_2H_5O_2^{\cdot} \rightarrow 2C_2H_5O\cdot + O_2$$

$$C_2H_5O\cdot + O_2 \rightarrow CH_3CHO + HO_2$$

$$M + C_2H_5O\cdot \rightarrow \cdot CH_3 + CH_2O + M$$

$$CH_3CHO + HO_2 \rightarrow CH_3\dot{C}O + H_2O_2$$

$$CH_3\dot{C}O + M \rightarrow \cdot CH_3 + CO + M \text{ (fast)}$$

$$\cdot CH_3 + O_2 + M \rightleftarrows CH_3O_2^{\cdot} + M$$

$$CH_3O_2^{\cdot}+C_2H_5O_2^{\cdot}\rightarrow CH_3O\cdot+C_2H_5O\cdot+O_2$$

$$CH_3O\cdot+O_2\rightarrow CH_2O+HO_2^{\cdot}$$

$$RO_2^{\cdot}+CO\rightarrow RO\cdot+CO_2 \qquad (6)$$

The overall stoichiometry in such a scheme is such that without considering propagation:

$$C_2H_6+\tfrac{5}{2}O_2\rightarrow 2CO+3H_2O_2$$

The auto-catalytic nature of the reaction could then be accounted for in terms of secondary initiation by RO_2H ($R = Me$ or Et) produced. If RO_2H decomposed into $RO\cdot+\cdot OH$, then each $\cdot OH$ could account for $3H_2O_2$ production via complete consumption of secondary products. It does not appear possible to reconcile the very high activation energies for $E_p(RO_2^{\cdot})$ with long chain lengths in the alkane oxidation. However, in all fairness, it must be pointed out that λ has never been measured in the alkane oxidations!

Knox has commented [2, 14], on the fact that in his studies there was no effect of alkane pressure on the alkene yield, such as would be required by the simple mechanisms, (2) and (4) [3]. However, Knox has covered a relatively small range in conditions where such effects are easily obscured. In their review article on oxidation, Medley and Cooley [9] have described very dramatic studies in which at 600 K the yield of C_2H_4 from C_2H_6 went from over 80 percent to zero on raising the pressure from 7 to 140 atm. Even at 600 °C ($\sim$900 K) and 140 atm, the C_2H_4 was only 46 percent. In similar fashion, at 265 °C and 150 atm pressure the yield of i-C_4H_8 from i-C_4H_{10} goes to zero and at 280 °C and 20 atm pressure, no C_3H_6 is detectable from $C_3H_8+O_2$.

4. Isomerization of $RO_2^{\cdot}$ Radicals

Some additional information on the activation energy from $RO_2^{\cdot}$ abstraction is provided by isomerization reactions. Baldwin et al. have made direct measurements on the rates of reaction of alkanes introduced in small amounts ($\leq$0.1 mole percent) into slowly reacting $2H_2+O_2$ mixtures at 480 °C. They follow RH disappearance and product appearance directly by GLC.

With neopentane, they find CH_4, 3,3-dimethyl oxetane, and i-butene, as major initial products. Acetone, C_2H_4, and C_3H_6 are all secondary products! There appears to be only one reasonable mechanism to account for this behavior:

$$(CH_3)_3C(CH_3) + X \xrightarrow{i} (CH_3)_3C-\overset{\cdot}{C}H_2 + XH$$

$$(X = O,H,OH)$$

$$(CH_3)_3C-\overset{\cdot}{C}H_2 \xrightarrow{i} i\text{-butene} + CH_3$$

$$+O_2 \underset{-2}{\overset{2}{\rightleftarrows}} (CH_3)_3C-CH_2OO\cdot \qquad (7)$$

From the initial measured rates of appearance of oxetane and olefin, respectively, the author estimates that $k_{oxet.}/k_{olef.}\approx10^{2.5}$ 1/mole (440 °C). But $k_{olef.}$ has been measured [10] at these conditions and is $10^{3.3\pm.3}$ s^{-1}. The half-life for oxetane under these conditions is about 70 seconds [11], which leads us to correct their ratio by a factor of 2 for lost oxetane to $10^{2.8}$ 1/mole. This then gives $k_{oxet.}\sim10^{6.1\pm.3}$ 1/mole-s.

Now, the steady state treatment of the mechanism gives:

$$k_{oxet.}=\frac{K_2K_3k_4}{1+k_4/k_{-3}+k_4K_3/k_{-2}}$$

There are three limiting cases for $k_{oxet.}$. If $k_4<k_{-3}$ and $k_3<k_{-2}$, then step 4 is rate limiting and

$$k_{oxet.}=K_2K_3k_4$$

If $k_4>k_{-3}$ but $k_3<k_{-2}$, then step 3 is rate limiting and $k_{oxet.}=K_2k_3$. Finally, if $k_4>k_{-3}$ and $k_3>k_{-2}$, step 2 is rate limiting and $k_{oxet.}=k_2$. We can estimate by analogy with Me and Et that $k_2\sim10^9$ 1/mole-s, so that this last possibility is about 10^3 too fast. From thermochemical data [12] we can estimate $K_2\sim10^2$ 1/mole at 750 K, so that in order for k_3 to be rate limiting, its rate would have to be $10^{4.1}$ s^{-1}. A_3 can be estimated at $10^{12.1}$ s^{-1}, which would require $E_3=28$ kcal/mole, an impossibly high value from any standpoint [13]. K_3 can be similarly estimated at $10^{-1.6}$ at 750 K, so that for the remaining case we conclude that $k_4=10^{5.7}$ s^{-1}. Since $A_4\sim10^{11.8}$ s^{-1}, this leads to $E_4\sim21$ kcal/mole with an uncertainty of about ±3 kcal/mole.

The comparable 3-membered ring epoxidation of the radical obtained from dtBP has an activation energy estimated at less than 16 kcal/mole, but its reaction is more exothermic (17 kcal versus 12 kcal).

One further piece of evidence on E_p comes from the relative isomerization rates of branched and unbranched peroxy radicals. Rust observed [14] that in the oxidation of 2,4-dimethylpentane in the neat liquid at about 150 °C, a 90 percent yield of 2,4-dihydroperoxide was formed. The ratio of mono- to diperoxide was about 1:10 and this has been since confirmed by independent measurements [15].

In direct contrast to this, the oxidation of n-octane is found to proceed with less than 10 percent of internal abstraction [15]. Since all peroxy radicals of n-octane can always find a γ-H atom to abstract, this suggests a factor of about 100, favoring internal abstraction in the case of the branched hydrocarbon over the unbranched. A factor of close to 10 can be accounted for by a higher A-factor for external abstraction for long chain unbranched alkanes compared to 2,4-dimethyl pentane. This arises from the statistical factor that it has only 2 abstractable H atoms per mole while n-octane has 14. But no set of activation energies, E_p, for H-abstraction by RO_2, high or low, can reconcile these data, and it must be assumed that at 120 to 150 °C, RO_2 abstraction from a secondary C–H position is sufficiently slow that other H-donors provide the propagation path and so inhibit internal abstraction.

A last point to consider in radical isomerization has to do with the reaction $O_2 + R \cdot \rightarrow HO_2 + olefin$. Knox [16] has suggested that this comes from a competition of isomerization and dissociation. For the $CH_3CH_2O_2$ radical, for example, he has suggested

$$C_2H_5 + O_2 \underset{-1}{\overset{1}{\rightleftharpoons}} CH_3CH_2OO\cdot$$

$$CH_3CH_2OO\cdot \underset{-2}{\overset{2}{\rightleftharpoons}} \dot{C}H_2CH_2OOH \overset{3}{\rightarrow} C_2H_4 + HO_2 \quad (8)$$
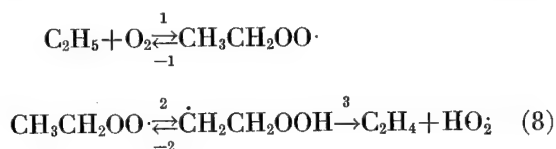
Now Baldwin et al. [7] have reported for reaction of C_2H_5, n-C_3H_7, and t-butyl radicals with O_2, almost quantitative reaction to give olefin $+HO_2$ with rate constants of 8.2×10^7 l/mole-s for C_2H_5 and 5.8×10^7 for n-propyl at 440 °C. If we assume these come from a direct metathesis reaction with an A-factor of about $10^{9.0}$ l/mole-s, this yields the quite reasonable activation energy of about 4 kcal/mole, in agreement with other observations at lower temperatures [17].

If, however, we interpret the rate in terms of the above isomerization and use 16 kcal/mole for the RO_2 primary H atom abstraction and a strain energy of 7 kcal in the 5-membered ring, we find that step 2 is rate determining with a rate constant, k_{olefin}, equal to K_1k_2. Since $K_1 = 10^{-5.0+27/\theta}$ at 600 K and with $k_2 \sim 10^{12.3-23/\theta}$ s^{-1} this gives $k_{olefin} = 10^{7.3+4/\theta}$. This becomes $10^{8.8}$ at 600 K and $10^{8.5}$ l/mole-s at 713 K, in disagreement with the observed data. To make the rates agree would require $E_2 = 25$ kcal/mole and make O_2 addition to $\cdot CH_2CH_2OOH$ faster than step 2. The value $E_2 = 33$ would result in a rate 10^3-fold too small! Another objection to the mechanism, which has already been noted, is that the predominant mode of decomposition for β-hydroperoxy alkyl radicals is via the epoxide, not the alkene. More details of this mechanism have appeared earlier [4].

5. Termination Reactions of Peroxy Radicals

Perhaps one of the largest discrepancies between gas-phase and liquid-phase oxidation studies comes from the termination reactions of peroxy radicals. For t-BuO_2 radicals, there is no termination in the gas phase. Termination in solution occurs via the trapping of a caged pair of t-$BuO\cdot$ radicals.

$$2t\text{-}BuO_2{}^\bullet \underset{-1}{\overset{1}{\rightleftharpoons}} (t\text{-}BuOOOOt\text{-}Bu)$$

$$(9)$$
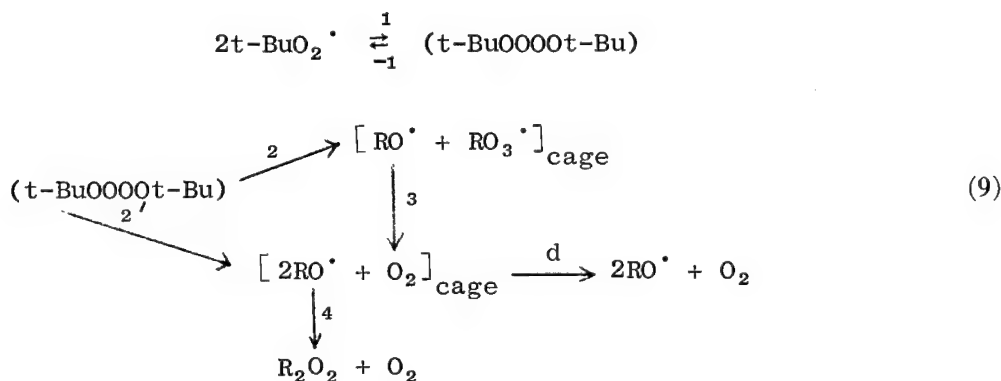
Recent ESR measurements by Ingold et al. [18] at low temperatures have given equilibrium constants and overall rate constants which are in good agreement with the thermochemical estimates [12] for steps 1, 2′, and 4. Their measurements suggest that the dissociation energy of the RO_2-O_2R bond is about 8 kcal/mole, rather than the value 6, estimated from bond additivity rules [12].

If, however, we turn to primary or secondary peroxides, the situation is not so good. They appear to have termination constants [19] appreciably higher than those for tertiary peroxy radicals. Thus, secondary radicals have $k_t \sim 10^6$ to 10^7 l/mole-sec, while primary radicals have k_t from 10^7 to $10^{8.3}$ l/mole-sec. It has been assumed by many authors that this arises from a cyclic complex transition state originally proposed by Russell [20].

$$2R_2CHO_2 \cdot \overset{a}{\rightleftarrows} (R_2CH)_2O_4 \overset{b}{\rightleftarrows} \left[\begin{array}{c} O \\ O \quad\quad O \\ R_2C \quad\quad\quad O \\ H \quad\quad CHR_2 \end{array} \right]^{\ddagger} \tag{10}$$

$$R_2C = O + O_2 + R_2CHOH$$
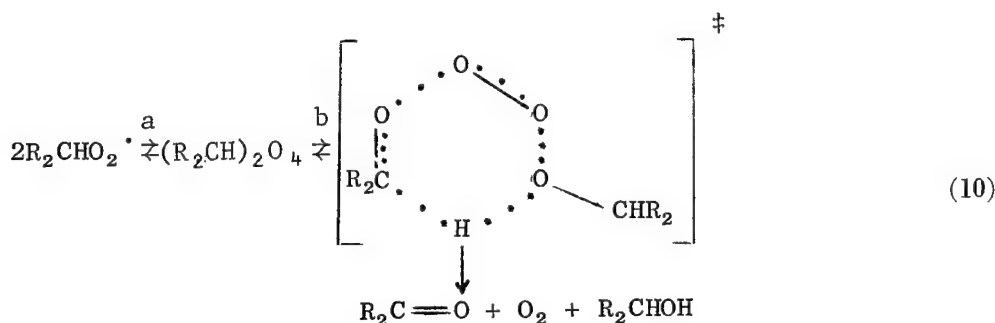
This is an analogue of the 1,5-H-shift reactions which have been much studied recently. The termination rate constant for such a mechanism would be given by:

$$k_t = \frac{k_b k_a}{k_{-a} + k_b} \nearrow \begin{array}{c} k_b \gg k_{-a} \to k_a \\ \\ k_b \ll k_{-a} \to K_a k_b \end{array}$$

From thermochemical data [11] the ΔS^0 for step a is -37.4 gibbs/mole, while the minimum entropy loss in step b accompanying the loss of 4 hindered rotors is 14.4 gibbs/mole and more likely 16.0 gibbs/mole [21, 22]. If step b is rate determining, this gives a maximum A-factor for k_t of $A_t = 10^4$ l/mole-s at 300 K and an expected value of $A_t = 10^{3.7}$ l/mole-s.

If we accept the data on K_a which give $\Delta H_a \sim 8$ kcal/mole, then the absolute values of the reported termination rate constants could only be reconciled with the thermochemical estimates, if $E_b \leq 1$ kcal/mole. However, under these circumstances $k_{-a} < k_b$ at $-40\,°C$ and step a, not step b, becomes rate limiting. This would also require a negative activation energy for recombination, which has not been observed.

A value of $E_b \leq 1$ kcal/mole would be extraordinarily low for a reaction which involves a 1,5-H-atom shift. On the other hand, the overall step is 58 kcal/mole exothermic even with $(^1\Delta)O_2$ as product, and we may have no adequate analogue for such an energetic reaction. Perhaps the main factor

mitigating against such a reaction is that it does not appear to occur in the gas phase. It is not out of the question that ionic, or at least very polar, reaction paths specific to solutions are involved in such steps, in which case the present type of analysis is irrelevant. Some indication in this direction is provided by the observation [23] that the pyrolysis of $(sec\text{-}BuO)_2$ yields about 30 percent H_2 in solution-phase pyrolysis. No such pathway or product has ever been observed in a gas-phase pyrolysis of a secondary peroxide, and it would seem to involve a solution-favored 6-centered transition state. Once again, the overall reaction is very exothermic (~ 60 kcal/mole).

H_2 evolution had been reported [24] in the decomposition of α-OH peroxides in solution, but these seem more likely to follow ionic pathways than simple peroxides or polyoxides.

6. Ozone Reactions

Although O atom and O_3 reactions are not of importance in oxidation reactions below 500 °C, they are of interest above these temperatures (e.g., in flames) and of special interest in the closely allied photochemical oxidations which occur in the upper atmosphere and in smog.

Recent studies [25] of the absolute rates of the gas-phase reactions of O_3 with C_2H_4 and with C_2H_2 have yielded the somewhat surprising results that the latter is appreciably less reactive than the former. The Arrhenius parameters for the bimolecular rates are:

$$k(C_2H_4 + O_3) = 10^{6.3 - 4.7/\theta} \text{ l/mole-s}$$

$$k(C_2H_2 + O_3) = 10^{9.5 - 10.8/\theta} \text{ l/mole-s} \tag{11}$$

These parameters for the C_2H_4 reaction are quite consistent with a concerted addition to form, exothermically, a 1,2,3-trioxocyclopentane which can then easily rearrange to form the 1,2,4-trioxide or ozonide. This has been discussed in some detail

[26] and it has been shown that a biradical intermediate $\cdot CH_2$–$CH_2OOO\cdot$ would require an activation energy in excess of 17.0 kcal/mole.

If the concerted path requires formation of a semi-ion pair transition state, then it is not easily understandable why acetylene doesn't react with nearly the same parameters as C_2H_4, since it appears to be reactive in concerted I_2 or HCl addition reactions [27]. Assuming that this is indeed the case, however, the reported parameters can then only be compatible with a biradical intermediate. For the reaction:

$$C_2H_2 + O_3 \underset{}{\overset{a}{\rightleftarrows}} \text{(structure)}$$
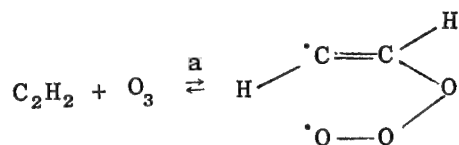
We can estimate from thermochemical data [21] that $\Delta H_a^0 \leq 11.7$ kcal/mole and $\Delta S_a^0 = -23.7$

gibbs/mole. The reported parameters (11) are consistent with these values, if we assume zero or small activation energy for the reverse reaction $(-a)$. In actual fact, the biradical may be partly stabilized by valence bond structures, such as:
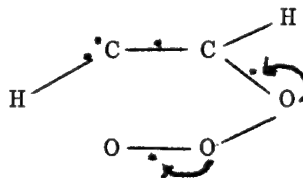
so that we have underestimated its ΔH_f^0 and step $(-a)$ may have some activation energy. If it does, the next step, which is 1,2,3-trioxocyclopentene formation, may be in competition with it. The final products appear to be compatible with the trioxide formation for C_2H_2, MeC_2H, and MeC_2Me. A generalized mechanism is:

(12)
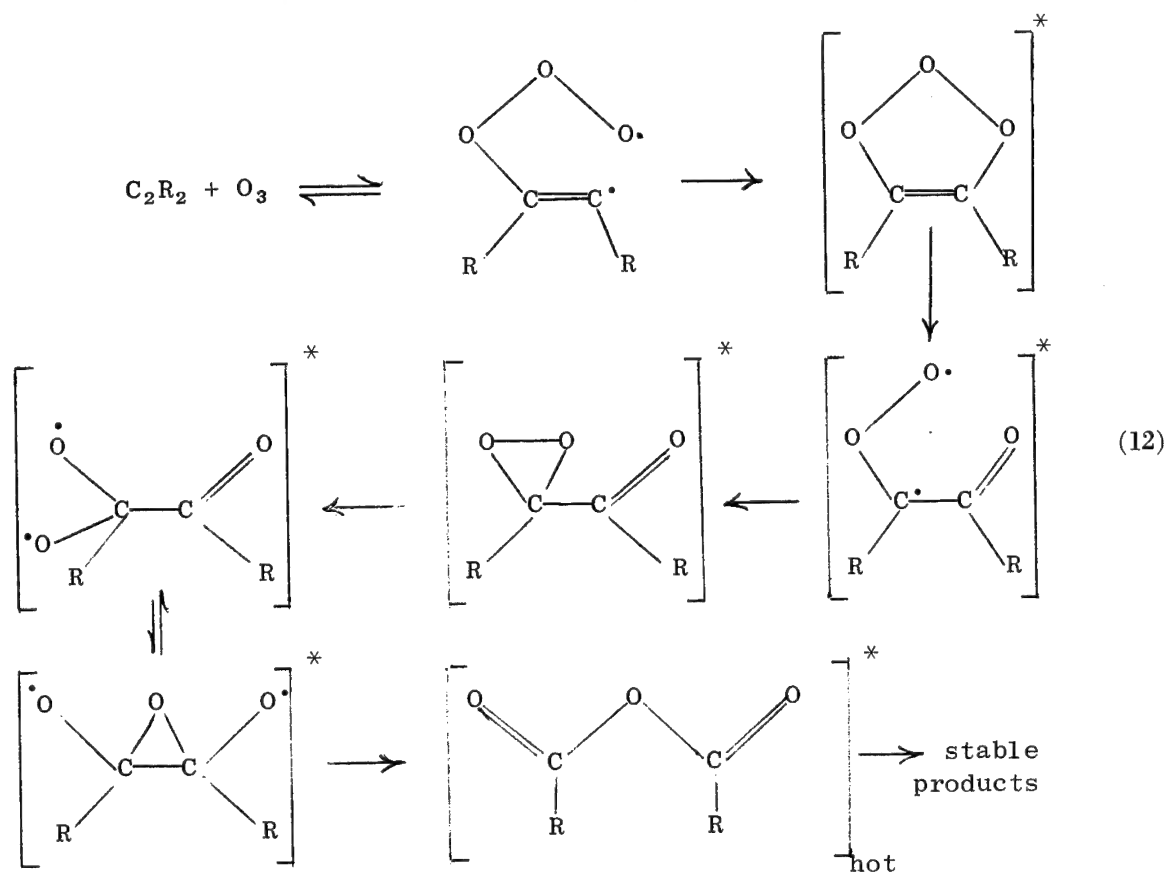
7. Effects of Surfaces on Oxidation and Pyrolysis

A recent work of interest in connection with the work on isomerization of peroxy radicals is that by Niclause et al. [28] on the effect of traces (0.5 to 5.0 percent) of O_2 on the oxidation of i-butane at 490 °C. These authors find that in the usual reaction systems of quartz or pyrex there is an initial fast reaction during which O_2 is consumed and after which the rate becomes the normal pyrolysis rate. With increasing surface, this acceleration decreases and it also decreases on coating the surface with PbO. With a very large surface/volume ratio and

PbO coating, there is attained a nearly zero O_2 consumption and vanishingly small pyrolysis rate!

If we assume that the O_2-free pyrolysis is largely homogeneous, then it appears that 1.0 percent of O_2 plus enough PbO surface can destroy essentially all the hydrocarbon chains. At the surface/volume ratio required to do this, it can be shown that CH_3 radicals will collide at the walls more readily than they will abstract H from the i-C_4H_{10}. H atoms, on the contrary, still abstract more readily than they collide with the walls. However, those radicals which can give rise to H atoms, t-butyl, will themselves strike the walls more readily than the competing reaction to form i-C_4H_8+H. Also, under the conditions employed the equilibrium, $\overset{a}{R\cdot+O_2\rightleftharpoons RO_2}$, is far to the left ($K_a\sim10^{-2}$ torr^{-1}) so that $(R\cdot)\gg(RO_2^{\cdot})$. The only exception to this is $H+O_2\rightleftharpoons HO_2$ for which $K_{eq}\sim10^7$ torr^{-1}. However, the formation of $HO_2^{\cdot}$ from H is very slow relative both to the abstraction $H+RH\rightarrow H_2+R\cdot$ and to collision with the walls. tBu$\cdot+O_2\rightarrow HO_2^{\cdot}+i$-$C_4H_8$ is slower than wall collisions.

We see that the striking inhibition by O_2+PbO surface of both the pyrolysis and the high temperature oxidation is consistent with a very efficient transformation of either t-butyl or CH_3 radicals into nonradical products. Since this occurs in the presence of about 0.5 torr O_2, but not in its absence, we must conclude that there is, in part at least, a surface reaction forming a surface species that is both stable at 700 K and capable of oxidizing alkyl radicals to molecular products. This is not $PbO_2(s)$ which is unstable relative to PbO under these conditions, but may be the very stable Pb_3O_4. The

authors note, however, that KCl covered surfaces have a similar behavior and conclude that it is the destruction of $HO_2^{\cdot}$ or $\dot{O}H$ at the walls which leads to the inhibition. $HO_2^{\cdot}$ is most probable.

Another finding of these authors is that under these extreme inhibiting conditions, the normal pyrolysis stoichiometry which produces about 71 percent i-C_4H_8+H_2 and 29 percent CH_4+C_3H_6, changes (at 1 percent O_2) to produce slightly more of the latter ($\sim$40 percent) while the H_2 is largely (90 percent) converted to H_2O and H_2O_2. The authors have attributed this to a more selective oxidation of H atoms or t-butyl radicals than CH_3 by O_2. The reaction tBu$\cdot+O_2\rightarrow i$-C_4H_8+$HO_2^{\cdot}$ either on the surface or in the gas phase could account for the H_2 oxidation. However, if we assume that the observed products still arise from gas-phase radical reactions, we must further account for a further rapid destruction of t-butyl radicals at the surface, since both H atoms and CH_3 radicals will still form about 50 percent each of t-butyl radicals and i-butyl radicals in abstractions from i-C_4H_{10}. i-butyl radicals, once formed, will split into CH_3+C_3H_6 more rapidly than they will strike the surfaces.

The observation on the small shift in stoichiometry can be understood if some nonselective radical, such as OH, is in part responsible for the observed products and/or, in addition, i-C_4H_8 is more easily destroyed than i-C_4H_{10} in the system. The latter is to be expected since i-C_4H_8 has six allylic H atoms which can be more readily abstracted by "sluggish" radicals, such as $RO_2^{\cdot}$. Once methyl-allylic radicals are formed, they may be expected to undergo oxidation by the following sequence:
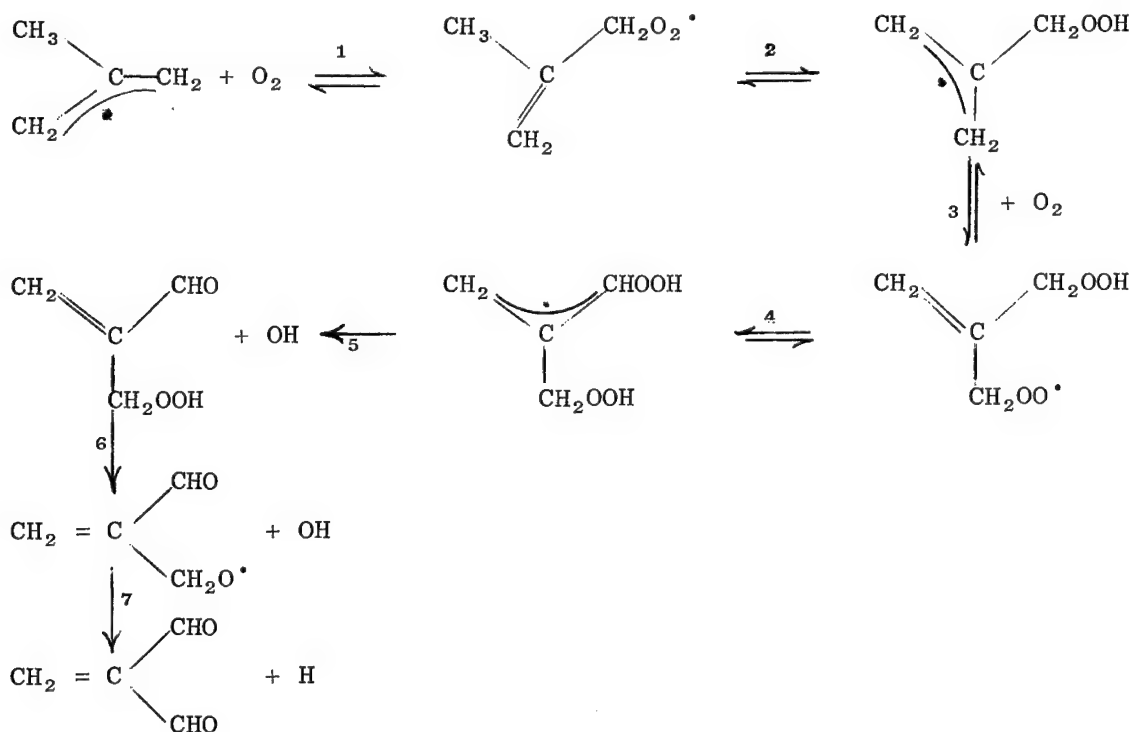
Despite the fact that the equilibria in steps 1 and 3 are very unfavorable for RO_2 formation ($K_1 \sim 10^{-4}$ torr^{-1} at 750 K), the competing isomerization steps (2 and 4, respectively) are as rapid as their inverse fission steps, so that one may expect further oxidation of the methyl-allyl radicals.

This sequence is peculiar to branched allyl radicals in contrast to unbranched, since only the former can undergo rapid internal isomerization via a 6-membered ring. CH_3–CH = CH–$CH_2OO\cdot$ radicals, for example, can only isomerize via a much less favorable 7-membered ring. The above sequence also produces the very reactive, nonselective, OH radicals which will react with parent i-C_4H_{10} more rapidly than they will diffuse to the walls and will also produce more i-butyl than t-butyl (3:2) radicals [29].

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Discussion

R. S. Konar (Catholic University):

Question 1:

Dr. Benson has estimated the energetics of the H-abstraction reactions by HO_2 radicals from paraffins containing primary, secondary and tertiary H atoms, (page 120 of preprints), and it follows that

$$k_p/k_t = 10 \exp(-5200/RT)$$

and

$$k_p/k_s = 10^{0.50} \exp(-2900/RT)$$

where k_p, k_s and k_t are the rate constants for the primary, secondary and tertiary H-atom abstraction reactions by HO_2 radical respectively.

In isobutane pyrolysis, (10 to 150 torr, 497 to 582 °C, R. S. Konar Ph.D. Thesis, Cambridge University, U.K., 1966), it has been found experimentally that

$$CH_3(\text{or, } H) + \text{iso-}C_4H_{10} \xrightarrow{k_t} CH_4(\text{or, } H_2) + ter\text{-}C_4H_9$$

$$\xrightarrow{k_p} CH_4(\text{or, } H_2) + iso\text{-}C_4H_9$$
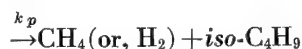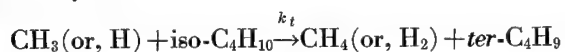
$$(k_p/k_t) = 10^{1.08 \pm 0.3} \exp[(-5500 \pm 1000)/RT]$$

While from propane pyrolysis, (Leathard, Ph.D. Thesis, Cambridge University, U.K. 1967; Leathard and Purnell, Proc. Roy. Soc. London. A 305, 517, 1968), it has been found that

$$k_p/k_s = 10^{0.62} \exp(-2700/RT)$$

for CH_3 or H atoms. It is evident that there is a good agreement between our experimental results and those of Dr. Benson's estimates. I wonder whether the ratio (k_p/k_s) or (k_p/k_t) could well be independent of the nature of the atom or radicals involved in the H-abstraction reactions in thermal systems.

Question 2:

In the decomposition of 'Chemically activated isobutane' (Simons et al., J. Chem. Phys. 52, 3911, 1970), it is believed that the reactions (a) to (d) will occur,

(a) $CH_2N_2 + h\nu \xrightarrow[O_2]{} {}^1CH_2 + N_2$,   ($\lambda = 4358$, or 3660 Å).

(b) ${}^1CH_2 + C_3H_8 \rightarrow \text{iso-}C_4H_{10}^*$ (vibrationally excited, 120 to 125 kcal/mole).

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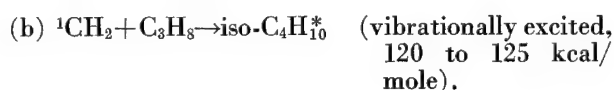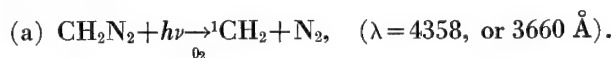
(c) iso-$C_4H_{10}^* \rightarrow CH_3 + $iso-$C_3H_7$
(d) iso-$C_4H_{10}^* + M \rightarrow $iso-$C_4H_{10} + M$

but not the reactions, (e) and (f),

(e) iso-$C_4H_{10}^* \rightarrow $ter-$C_4H_9 + H$
(f) iso-$C_4H_{10}^* + O_2 \rightarrow $products.

There was incomplete product analysis, and the authors simplified the situation by pumping out the noncondensables at the liquid nitrogen temperature. If (d) occurs, why not (f)? I wonder whether Dr. Benson would make some comments on this oxidation process (f) at 298 K.

S. W. Benson:

1. I think the striking parallel between relative rates of attack on primary, secondary, and tertiary H-atoms by CH_3 and HO_2 is just a fortuitous circumstance. Very selective radicals like I atoms and Br atoms will show about the same behavior while very unselective species like F, Cl, OH, and NH_2 will probably show little or no difference in activation energy and only a statistical difference in H-factors of $3:2:1$.
2. One can estimate using RRK or RRKM theory, the relative rates of disappearance of a chemically activated species via each of several competing routes. For two competing paths 1 and 2 with Arrhenius parameters $A_1 e^{-E_1/RT}$ and $A_2 e^{-E_2/RT}$, this ratio is:

$$\frac{\text{Rate (path 1)}}{\text{Rate (path 2)}} = \frac{A_1(E-E_1)^{s-1}}{A_2(E-E_2)^{s-1}}$$

where s is the effective number of internal oscillators in the excited species.

For the paths c and e suggested by Dr. Konar, $E_c \sim 80$ kcal/mole and $A_c \sim 10^{16.5}$ s^{-1} while $E_e \sim 91$ kcal/mole and $A_e \sim 10^{14.5}$ s^{-1} so that path e will never be seen.

The competing path F won't be seen for other reasons, namely that its A-factor is about $10^{8.5}$ 1/mole-s so that even if it has no activation energy,

it is unlikely to compete with the much faster bimolecular step d which has a rate constant of about 10^{11} 1/mole-s.

What does surprise me is that the authors do not report the more favored path:

$$i\text{-}C_4H_{10} \xrightarrow{g} i\text{-}C_4H_8 + H_2$$
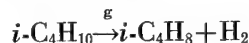
which has $E_g \sim 75$ kcal/mole and $A_g \sim 10^{13.8}$ s^{-1}.

M. H. Back (University of Ottawa):

I would like to ask Professor Benson whether the large difference in activation energy which he points out between the hydrogen abstraction reactions of the t-butylperoxy radical and the HO_2 radical is also observed in the termination reactions of the two radicals. He mentioned an activation energy of about 8 to 10 kcal/mole had been measured for the termination of t-butylperoxy radicals. If the HO_2 radicals terminate with no activation energy then the large difference would appear to persist in the termination reactions. Such a difference would then seem to have some basis in the structural or other differences between the two radicals. On the other hand if the activation energy for termination is the same for both radicals then the observed differences in the abstraction reactions can probably be attributed to experimental error or other artefact.

S. W. Benson:

The disproportionation of HO_2 radicals has never been measured directly and its rate constant has been estimated from very complex overall kinetics in the $H_2O_2 + H_2 + O_2$ system. It appears to be similar to the disproportionation of C_2H_5 radicals but about 3-fold slower. Like alkyl radical disproportionation, it does not appear to have an activation energy. $tBuO_2$ radicals cannot terminate in the gas phase. In solution they form $2tBuO\cdot + O_2$ in a solvent cage, and the small amount of observed termination is due to this latter mode (eq 9). No such cage recombination can occur in the gas phase.

Kinetics and Mechanisms of Flames and Flame Suppression*

R. M. Fristrom

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Md. 20910

A survey is given of the processes important in gase phase combustion with emphasis on chemical kinetics.

Gas phase combustion processes are important to the burning of polymers because the major exothermic reactions occur there. The combustion of many plastics can be roughly divided into a pyrolysis stage occurring at or close to the surface producing combustible gases and a gas phase oxidation stage in the surrounding atmosphere where the evolved gases are burned. Since the pyrolysis is usually endothermic, it is driven by the heat transferred from the gas phase flame by conduction and radiation.

Reaction schemes are outlined for some typical simple gas phase flames and these are related to the complex chemistry of the polymer combustion. A discussion is given of possible mechanisms for gas phase flame inhibition. Sources of information on chemical kinetics are listed and a bibliography is given of compilations of gas phase chemical kinetic rate parameters.

Key words: Chemical kinetics; combustion, gas phase; flame kinetics; flame mechanisms; flame suppression; inhibition; suppression.

1. Introduction

This survey presents an outline of combustion processes with an emphasis on the kinetics of gas phase flames and flame inhibition. Models will be outlined and sources of transport thermodynamic and kinetic information given. Gas phase reactions are important to the oxidation of organic solids because the major exothermic steps appear to be located there. Simplistically, one may look upon a burning solid (liquid) as a fuel source for a gas phase flame. The flame in turn feeds back thermal energy and reactive species to induce gasification. Gas phase combustion and condensed phase degradation are thus strongly coupled. The elementary processes of gas phase combustion are well understood and much quantitative information is available. Flame mechanisms have been intensively studied and some of the simpler flames are quantitatively understood [1, 2].[1] The surface phenomena in the oxidation of organic materials are complex and less well understood.

2. Combustion Processes and Models

Fire is the common term for combustion, especially when it is uncontrolled. Combustion is an exothermic reaction, usually an oxidation, which has the ability to propagate through space. Reaction requires that the fuel and oxidizer be mixed on the molecular level and that a source of ignition be present. Fires may be classified according to: (1) the initial phases of the fuel and oxidizer; (2) the character of the initial distribution of fuel and oxidizer; and (3) the dominant processes by which mixing occurs. The propagation of such systems may be limited by reaction rates, by mixing rates, or by the external rate of introduction of fuel or oxidizer (fig. 1). Detonations may be considered a special case of fire in which the reaction processes are so rapid that the propagation rate is supersonic relative to the cold reactants.

A number of strongly coupled chemical and physical processes are involved. They fall into three categories: (1) heat transfer, (2) overall mass transfer, and (3) species transfer. Heat can be transferred by convection, thermal conduction, and radiation. Mass can be transferred by convection and molecular diffusion. Species transfer, or exchange, as distinguished from overall mass transport, can be accomplished by turbulent transport, molecular diffusion, and chemical reaction. Chemical reaction furnishes the energy source in fires and is, therefore, the ultimate driving force.

In the gas phase fires are referred to as flames. Flames are an important component of most fire systems because the exothermic stages of reaction are usually located in the gas phase. This seems intuitively reasonable because mixing is most easily accomplished in the gas phase. Therefore, unless a system is deliberately premixed, reaction will concentrate in the gas phase or at a boundary between two phases. A contributing factor is the slowness of diffusion as compared with thermal conduction in condensed phases. This sharply reduces the transport of active species. Thermal flames are possible in such systems, but intimate mixing is required. As a result,

[1] Figures in brackets indicate the literature references at the end of this paper.

INITIAL PHASE	INITIAL MIXING	
	PREMIXED	NON-PREMIXED
GAS-GAS	LABORATORY BUNSEN FLAME	GAS FURNACE
GAS-LIQUID	MIST EXPLOSIONS[a]	OIL BURNER
GAS-SOLID	DUST EXPLOSIONS[a]	COAL FURNACE
LIQUID-LIQUID	METHL NITRATE[b] DECOMPOSITION FLAME	LIQUID O_2 KEROSENE ROCKET MOTOR
LIQUID-SOLID	FUEL OIL-NH_4NO_3 EXPLOSIVE	H_2O_2—POLYETHYLENE HYBRED ROCKET MOTOR
SOLID-SOLID	TNT[b]	GUN POWDER

(a) COLLOIDAL DISPERSIONS

(b) THESE ARE SPECIAL CASES IN WHICH FUEL AND OXIDIZER ARE GROUPS ON THE SAME MOLECULES. MANY SUCH MATERIALS CAN BE DETONEATED.

FIGURE 1. *Examples of types of fires.*

most condensed phase flames are of the decomposition type where the oxidizer and fuel occupy the same molecule. They produce detonations when the pressure drop from rapid volatilization of a solid (liquid) produces supersonic flow. Most species will be gaseous at the temperatures involved.

The combustion of liquids and solids is often limited by the gasification mechanism. This may be: vaporization (sublimation), or pyrolysis. Pyrolysis can result from pure thermal decomposition or be induced by chemically active species.

The most common fuels are compounds of hydrogen-carbon and the most common oxidizer is atmospheric oxygen. Other combinations, however, are combustible [3, p. 29].

2.1. Flames

Flames are gas phase chemical reactions with the ability to propagate through space. This results from a coupling between chemical reaction and molecular transport. To produce gradients sufficient for coupling, a reaction must be rapid compared with transport processes. This is usually rapid by laboratory standards. As a result flames are localized in space. The reaction region is called flame front, reaction wave, or reaction zone.

There are many types of flames (fig. 2). Most, though not all, flames occur in the gas phase. They can be classified according to the character of the mixing process which must take place before reaction. Thus one has: decomposition flames where the oxidizer and fuel occupy the same molecule; premixed flames where the fuel and oxidizer are premixed on the molecular level; diffusion flames where fuel and oxidizer mix by diffusion; and turbulent flames where they mix through eddy diffusivity. Since final mixing must be on the molecular level, the reaction zones of these flames of differing appearance involve the same basic physical and chemical processes. They differ only in the mode of introduction and removal of species (fig. 3).

Flames can be quantitatively described by a set of equations [3, (p. 74), 4], combining the mechanics

of the fluid flow with the constraints of conservation of energy, conservation of atomic species, and conservation of momentum, and the differential equations describing: molecular diffusion, thermal conduction, thermal diffusion, and chemical reaction. This set of simultaneous differential equations form a boundary problem [4] in which the rate of propagation (commonly called burning velocity) plays a role of eigenvalue. In the general case the eigenvalue is a tensor which is both space dependent (diffusion flames), and/or time dependent (turbulent flames). This is very difficult to visualize.

2.2. Premixed Flames

The simplest form of the flame equations is the one-dimensional, time-independent case [3, 4]. This quantitatively describes most premixed laboratory flames [3]. The eigenvalue can be identified with the propagation rate (commonly called burning velocity). These flames conform to the geometry imposed by the flow system balancing the burning velocity with the local component of inlet gas flow (fig. 4).

2.3. Flame Reaction Zone Structure

All of the processes important to the general case occur, with the exception of the time dependence, which can become important in ignition, extinction, and in turbulent flames.

The chemistry of flames is complex, although the reactions are principally those of a limited number of radical species (H, O, OH, and CH_3 in the carbon hydrogen-oxygen system).

Several simplifying approximations appear applicable to many flame reaction zones. (1) There is a dominant pair of reaction paths (one for the oxidizer,
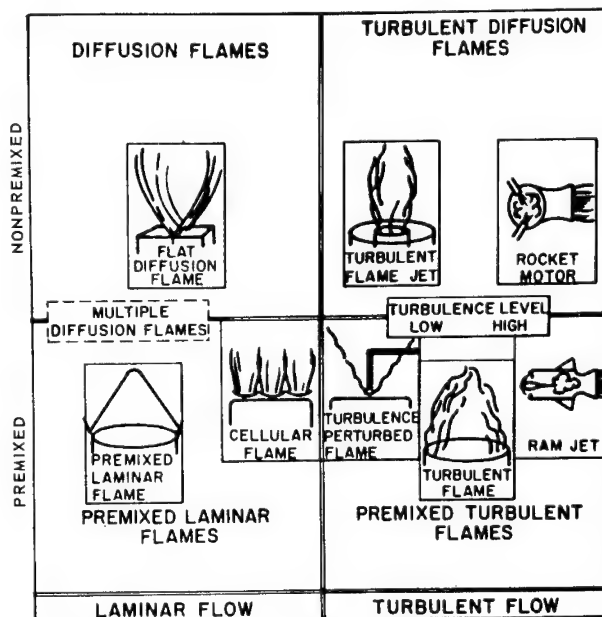
FIGURE 2. *Examples of flame types.*

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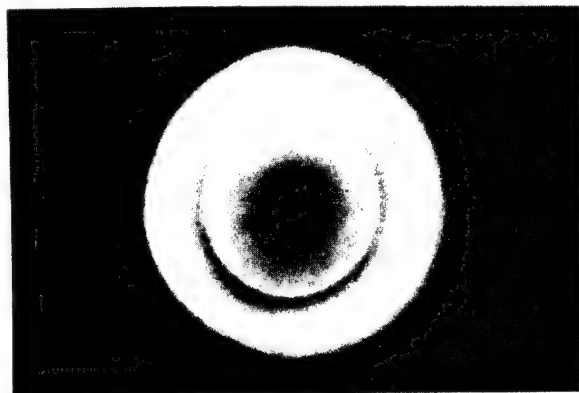
(a) PICTURE 1/10 Atm 0.08 CH_4–0.92 O_2
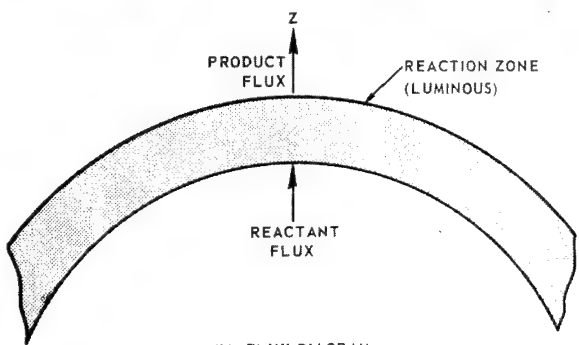
(b) FLUX DIAGRAM
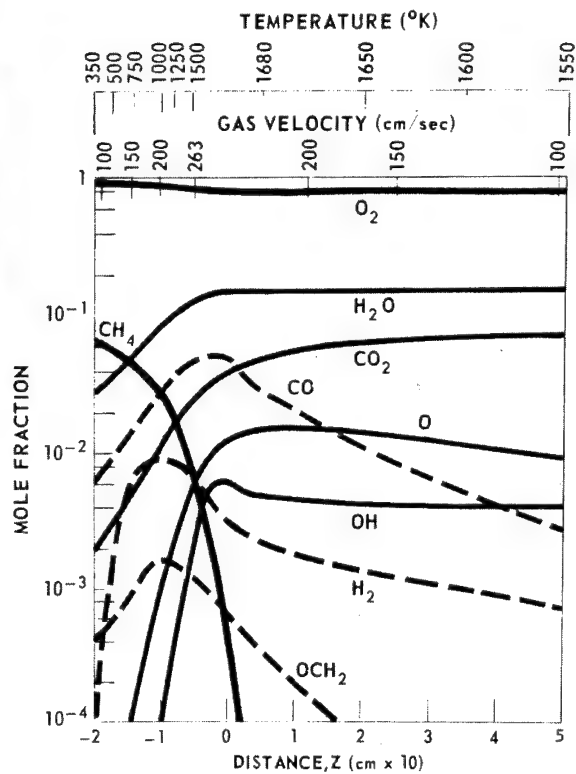
(c) MICROSTRUCTURE

FIGURE 3A. *The structure of simple flames—Premixed laminar flame.*

(a) PICTURE 1/10 ATM CANDLE FLAME
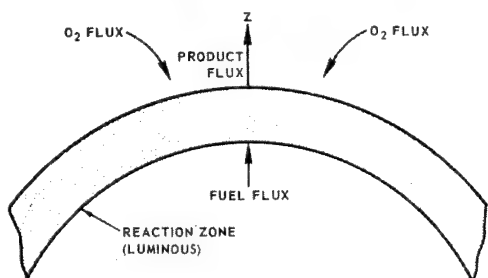
(b) FLUX DIAGRAM
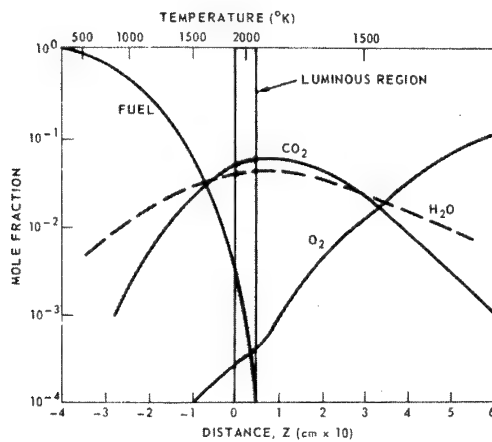
(c) MICROSTRUCTURE (schematic)

FIGURE 3B. *The structure of simple flames—Laminar diffusion flame.*

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(a) TURBULENT FLAME BALLS 1 ATM STOICHIOMETRIC C_3H_8–AIR

(b) INSTANTANEOUS DIAGRAM OF REACTION REGION

(c) MICROSTRUCTURE (schematic)
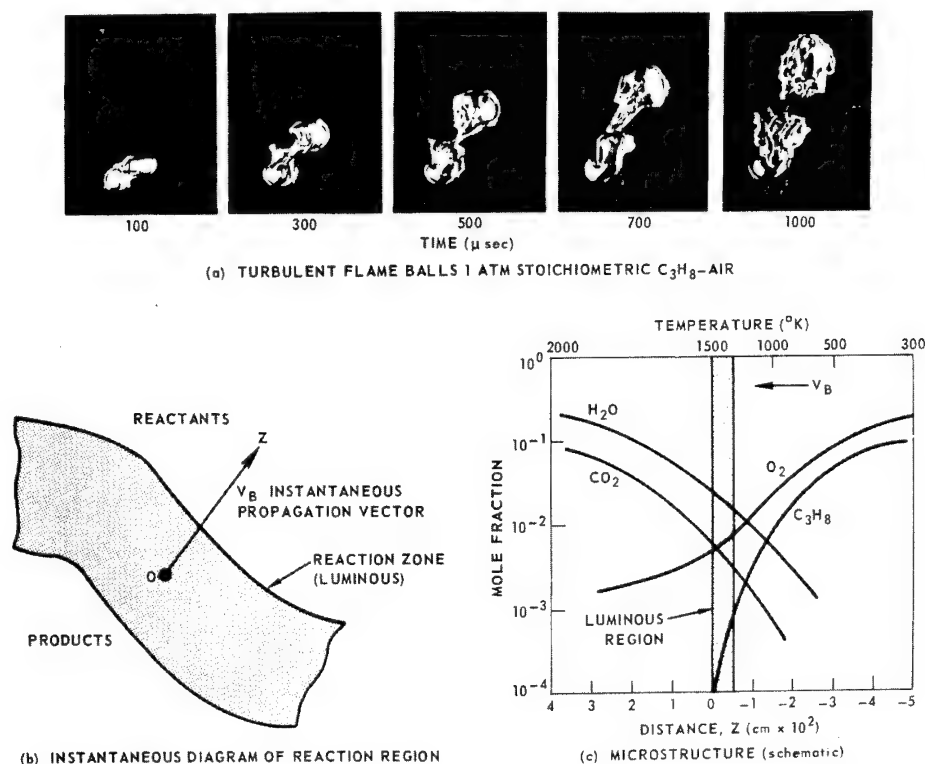
FIGURE 3C. *The structure of simple flames—Turbulent flame (premixed).*

one for the fuel). (2) In the sequential reaction path one may find several spatially separated stages coupled principally by convection. (3) In each stage reaction will be concentrated at the hot boundary. (4) Propagation rate is controlled by the slowest step in the most rapid path. Details of the arguments leading to these conclusions may be found in [5].

3. The Thermodynamics of Combustion

Thermodynamics deals with the equilibrium properties. Flames are approximately adiabatic overall, and precise thermodynamic data are available which allow reliable calculations to be made of the temperatures and compositions of most common flame systems. The calculations are straightforward, but chemical complexity and the presence of radicals in the high temperature gases preclude writing stoichiometric relations without a prior knowledge of the flame temperature. The calculations must be made iteratively.

Two equivalent formulations have been developed for calculations: the equilibrium constant method, and the free energy minimization method. The former is found in many texts [6]. The latter is a recent development. Machine programs are available for both methods [7, 8]. The most reliable source of data for such calculations is the JANAF Tables [9]. Machines make these tedious calculations economically in a few seconds.

The insight provided by thermodynamic calculations is useful for predicting combustion gas properties, evaluating fire hazards [10], and in simple flame theories [5]. Nonequilibrium systems often can be treated by truncation to calculate partial or frozen equilibria [2, p. 34], in which only certain reactions are allowed to go to completion. Such calculations are useful in estimating the properties of systems, such as turbulent flames, rocket nozzles, and flame reactions.

4. Transport Properties

An understanding of fire systems requires a quantitative knowledge of transport processes. These are: thermal conduction, the transport of heat by temperature gradients; and diffusion, the transport of matter by temperature gradients and the second order processes, thermal diffusion, and diffusion thermal effects.

Viscosity is unimportant in flames (but important in detonations); thermal diffusion is important for very light species (H, H_2 and He), and the diffusion thermal effect is negligible. A discussion of these processes and compilation of data for use in gas phase flame calculations can be found in [2 and 11]. In condensed phases diffusion is negligible on the time scale involved in fires and by comparison with thermal conduction. Collections of evaluated transport information for condensed phases can be obtained from [12].

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5. Combustion Kinetics

The energy source of combustion systems is chemical reaction. The time history and characteristics of flames and fires are controlled by the kinetics of the reactions. This branch of chemistry involves the study of the rates and detailed paths by which chemical reactions occur. The discussion can be conveniently divided into two parts: the mechanisms or qualitative description, and the elementary rate constants which provide the quantitative data. Mechanisms can be given on three levels: the overall stoichiometric description, often called global reaction; the elementary reaction scheme; and the chemical dynamic level which describes the detailed internal processes and energy levels involved in reaction. At present the first two levels are the most useful for combustion systems. The goal of any mechanism is to provide a quantitative description of a reacting system. The difference between these three levels can be appreciated by considering the hydrogen-oxygen flame reaction.

The "global" or stoichiometric description indicates that two molecules of hydrogen and one molecule of oxygen are converted into two molecules of water, and the rate is a function of the concentrations and temperature.

$$R_{H_2+O_2} = f(H_2, O_2, T) \text{ e.g., } \approx H_2^a O_2^b T^c \qquad (1)$$

This is an empirical result and should not be extrapolated beyond its region of validation.

The elementary reaction formulation uses a detailed mechanism of elementary steps. For example, in combustion systems molecular hydrogen does not react directly with molecular oxygen. For the hydrogen-oxygen system the accepted mechanism is a set of six forward and reverse reactions (table 2). This requires six reaction rate parameters and six equilibrium constants for the reverse reactions.

$$R_{H_2+O_2} = f(k_1 \ldots k_6; K_1 \ldots K_6; N_1 \ldots N_n; T)$$
$$= f(R_1 \ldots R_n) \qquad (2)$$
$$R_i = [i][j]k_{ij}$$

where

R = Rate of Reaction
k = Rate Constant
K = Equilibrium Constant
N = Concentration
i, j, k = Indices

The virtue of this formulation is that the functional forms are known (see below).[2] Since this

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[2] Bimolecular chemical kinetic rate constants are normally given in the Arrhenius form:

$$k_{ij} = A_{ij} T_{ij}^{b_{ij}} \exp(-E_{ij}/{}^*RT)$$

Because of the exponential relationship dependence of reaction rate on temperature, most experimental data is not of sufficient precision to allow the reliable determination of b and it is often set arbitrarily at zero.

Termolecular reactions show a much lower negative temperature dependence. They are often fitted to a power law:

$$k_{ij} = A_{ijk} T^{-m}$$

These rates show a cubic dependence on pressure. In these equations: A = Frequency Factor; E = Activation Energy; k = Rate Constant; m = Temperature Exponent; $^*R$ = Molar Gas Constant; T = Temperature.

description is not empirical, it can safely be extrapolated outside the temperature or time area of study. The difficulty with the method is that many more variables (concentrations) are involved, which often are implicit functions not only of other species, but also time and temperature. In many cases parameters for the steps may not be available. The complexity of such a description usually exceeds the empirical global formulation. In favorable cases it is possible to reduce this complexity [5], but this is an art. Often the description is amenable only to machine processing. This should not always be a deterrent since the complexity is simply one of numbers of items, and the capacity of modern computers has been doubling every eighteen months for the last two decades and shows every prospect of continuing this trend [13]. Therefore, the elementary reaction attack on flame problems should ultimately prove the most fruitful approach.

The chemical dynamic level involves the specification of the reaction rate or cross-sections for the individual states of the molecules involved. This detail is available for very few systems. An example is the reaction of hydrogen atoms with molecular bromide [14], where the distribution between the various excited states is known.

$$k[H+Br_2] = k_1[H+Br_2 \rightarrow HBr_{v \leq 4} + Br^*({}^2P_{1/2})]$$
$$+ k_2[H+Br_2 \rightarrow HBr_{v \leq 6} + Br^*({}^2P_{3/2})] + \ldots \qquad (3)$$

This detail is available for so few systems that at present its utility is severely limited. As such studies become more common they may provide considerable information on nonequilibrium radiation. The description is even more complex than the elementary reaction schemes since each individual state of a molecule (vibrational, rotational, and electronic) is considered a separate species. It seems probable that by the time sufficient data are available for use in practical systems, the data handling capabilities will have expanded sufficiently to accommodate the information. The practical utilization of such detail appears to be a number of decades away.

There are three aspects of flames: ignition, extinction, and propagation. These areas share a common chemistry since the set of elementary reactions required for a complete description depends only on the species involved. In practice, when one wishes to select a quantitative mechanism with a minimal number of reactions, the reaction conditions differ sufficiently so that it is convenient to discuss their mechanisms separately. The complexity and availability of information varies from area to area so the coverage will be rather unequal. The elementary rate data are applicable to all of the

areas so they will be discussed separately from the mechanisms.

Flames can be ignited by thermal means and by active species transfer. In thermal ignition a critical volume of gas is raised to the point of thermal explosion [15] where heat is generated more rapidly than it can be dissipated. This may be done by external heating by a hot surface or by internally generated heat. The latter process is known as spontaneous ignition. Since the system passes continuously from cold gas to flame temperature with many intermediates, the chemistry is complex and time dependent. The hydrogen-oxygen thermal ignition is moderately well understood [15], but other systems are more complex and less well understood. In the case of carbon-hydrogen-oxygen system oxygenated intermediates and peroxy radicals play important roles. The area of hydrocarbon oxidation has been surveyed [16]. Ignition by transfer of active species occurs in spark ignition or direct contact with a pilot flame. In both cases high temperatures and radical concentrations are involved. This chemistry is similar to that of propagating flames discussed below. Low temperature ignition by radicals is probably possible, but is a less common occurrence.

Propagating flames involve principally the high temperature chemistry of a restricted number of radical species. In the carbon-hydrogen-oxygen system these are H, O, OH, and CH_3. Flames involving the chemistries of compounds containing nitrogen, sulfur, boron, etc., have received less study.

The chemistry of flame extinction involves reactions which reduce the concentrations of active radical species. Active radical concentration can be reduced by three body recombination, by surface recombination, or by substitution of an unreactive for an active radical species. This is usually accomplished by the addition of particles (for surface recombination) or by the addition of foreign species which promote recombination or substitution. The particles are generally alkali metal salts which may promote heterogeneous reactions. Foreign species are commonly halogen or halogen containing compounds so that hydrogen-halogen chemistry is important. This area is not completely understood although a number of important reactions have been identified [17].

5.1. Reaction Mechanisms

The best understood flame chemistry is that of steady state premixed flames of the carbon-hydrogen-oxygen system. This involves the high temperature reaction of H, O, OH, and CH_3. The system is most easily visualized as a hierarchy of reactions. Since oxygen is a divalent radical, one must consider the chemistry of both oxygen atoms and hydroxyl radicals. The high temperatures in flames appear to make ozone, hydrogen peroxide and HO_2 radicals quantitatively unimportant. In addition, hydrogen atoms and methyl radicals must also be considered.

Present evidence indicates that hydrocarbon and peroxy radicals, with the exception of CH_3, are thermally unstable under flame conditions. Hydrocarbon radicals can be important in low temperature oxidations and ignitions; and HO_2 radical is important in ignition and perhaps in low temperature hydrogen flames.

5.2. The Ozone Decomposition Flame

This is the simplest flame which can be realized in the laboratory. Three species are involved and the reactions can be written by inspection (table I).

Because of its simplicity it is the favorite of the theoreticians. There is reasonable agreement between measured burning velocities and computations based on elementary rates.

TABLE I. *Ozone flame*

[See Table VIII, #3, 15, 17, 20, for sources of kinetic constants]

$$O_3 + M^* \rightleftarrows O + O_2 + M$$
$$O + O_3 \rightleftarrows 2O_2$$
$$O + O + M \rightleftarrows O_2 + M^*$$
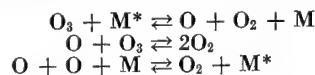
5.3. The Hydrogen Oxygen Flame

Eight reactions are required to describe this intensively studied flame. They can be written by inspection and most of them have received some study. The mechanism assumes that H_2O_2, O_3 and HO_2 are quantitatively absent. This would be expected from their low thermal stability. Detailed flame studies have confirmed this assumption except in the case of certain low temperature, high pressure flames where HO_2 reactions become important [18] (table II).

TABLE II. *Hydrogen oxygen flame*

[See Table VIII, #3, 17, for sources of kinetic constants]

$$H + O_2 \rightleftarrows OH + O$$
$$H + H_2O \rightleftarrows H_2 + OH$$
$$O + H_2 \rightleftarrows OH + H$$
$$H + O + M \rightleftarrows OH + M^*$$
$$H + OH + M \rightleftarrows H_2O + M^*$$
$$O + H_2O \rightleftarrows 2 OH$$
$$H + H + M \rightleftarrows H_2 + M^*$$
$$O + O + M \rightleftarrows O_2 + M^*$$
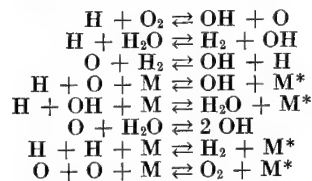
5.4. The Carbon Monoxide Flame

A key peculiarity of this flame system is its negligible propagation rate in the absence of traces of a hydrogen containing compound. This catalysis is independent of the molecular form, water being as effective as hydrogen in trace amounts [2]. This implies that reaction of CO with O is slow under flame conditions and the principle attack of CO must be by hydroxyl radicals. Thus a scheme for the carbon monoxide flame should include the reactions of the

TABLE III. *Carbon monoxide flame*

[See Table VIII, #2, 3, 17, for sources of kinetic constants]

$$CO + OH \rightleftarrows CO_2 + H$$

hydrogen oxygen system and an additional reaction for the attack of CO (table III).

5.5. Hydrocarbon Flames

The chemistry of hydrocarbon flames is complex, but the general outline seems clear. Complications include the differing chemistries of fuel lean and fuel rich systems; the effect of changing chain length in an homologous species; and the effect of unsaturation. Saturated hydrocarbons show substantially similar burning velocity curves if compositions are expressed in terms of the stoichiometry. As might be expected agreement is poor for methane and highly branched compounds which have rather different C–H ratios. Unsaturated compounds burn more rapidly than their saturated analogs, but the effect is less pronounced in the higher weight molecules. In fuel lean systems one finds as intermediates only hydrocarbons which can be obtained from the parent fuel molecule by degradation. Fuel rich flames by contrast show intermediates higher in molecular weight than the parent fuel. This is, no doubt, connected with reactions of methyl radical which is stable in such environments.

A correlation between hydrogen atom concentration and burning velocity has been discussed at length in the literature [19]. It appears to apply to hydrogen, carbon monoxide and saturated hydrocarbon flames and less well to olefin and acetylenic flames [17]. An interpretation of these facts which appears reasonable is that the reaction of oxygen, which is common to all of these systems, is principally with H atoms [2, 20]. This is the principle branching step which furnishes the radicals which are necessary for flame propagation, and it is the limiting slow step which controls the propagation rate [2, 5].

In fuel lean hydrocarbon flames the initial attack of the molecule appears to be by hydroxyl radical forming water and the corresponding radical. Hydrocarbon radicals higher than methyl are thermally unstable under flame conditions and appear to undergo unimolecular decomposition rather than radical attack. Two modes of decomposition occur: a fission into a radical and an olefin and splitting to form methyl radical and an olefin. This breakdown continues so that final oxidation is principally of ethylene and methyl radicals.

Fuel Lean Hydrocarbon Attack [See table VIII, #22 for sources of kinetic constants]

$$C_nH_{2n+2} + OH \rightarrow H_2O + \cdot C_nH_{2n+1}$$

$$\cdot C_nH_{2n+1} \rightarrow \cdot CH_3 + C_{n-1}H_{2n-2}$$

$$\cdot C_nH_{2n+1} \rightarrow \cdot CH_{2m+1} + C_{n-m}H_{2(n-m)}$$
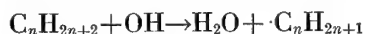
In fuel rich hydrocarbons hydrogen atoms are the dominant radical and attack the hydrocarbon. The formation of hydrocarbons higher in molecular weight than the fuel are observed in such flames. This is attributed to the low concentrations of oxidizing species and the concentration of methyl radicals can be quite high and additional reactions can take place.

Fuel Rich Hydrocarbon Attack [See table VIII, #22 for sources of kinetic constants]

$$C_nH_{2n+2} + H \rightarrow H_2 + \cdot C_nH_{2n+1}$$
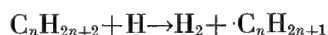
Olefins undergo the same radical attack sustained by saturated hydrocarbons, but in addition they can be attacked at the double bond by oxygen atoms. In ethylene flames this appears to result in the formation of formaldehyde which in turn is rapidly attacked by hydroxyl radicals or oxygen atoms with the formation of carbon monoxide.

Acetylenic compounds also can be attacked by oxygen atoms at the site of the triple bonds; again in acetylene flames some formaldehyde is formed. The mechanism of these reactions is not presently clear.

Unsaturated Hydrocarbons [See table VIII, #23 for sources of kinetic constants]

$$H, OH + C_nH_{2n} \rightarrow H_2, H_2O \cdot C_nH_{2n-1}$$

$$O + C_nH_{2n} \rightarrow CH_2O + C_nH_{2n-2}$$

$$H, OH + C_nH_{2n-2} \rightarrow H_2, H_2O + \cdot C_nH_{2n-3}$$
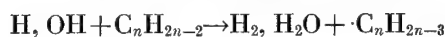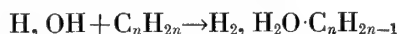
5.6. The Inhibition of Flames by Halogen Compounds

Flames and fires can be inhibited or extinguished by the introduction of halogen containing compounds. The effect of these species is so pronounced that the action is assumed to be chemical rather than physical [17]. It appears that the principal action is the modification of radical concentrations and/or distribution in the reaction zone. This interferes with the propagating and branching steps. Halogen compounds appear to act by substituting a radical of low reactivity for the propagating radicals.

Typical inhibitors are the halogens, or halogen substituted hydrogen or carbon compounds. Corrosion and toxicity considerations limit practical extinguishments to halogenated hydrocarbons (e.g., CF_3Br). The chemistry of halogenated hydrocarbons includes that of the halogens and halogen acids. The effectiveness of these inhibitors appears to be in the order of decreasing reactivity of the atom species, $F < Cl < Br < I$, and is proportional to the number of halogen atoms in the inhibitor molecule. Fluorocarbon radicals also appear to function as unreactive radical exchange species.

All of the halogens, with the exception of iodine, can sustain hydrogen flames. The reactions for these systems are similar and can be written by inspection (table IV).

Halogen molecules and the halogen acids (excepting fluorine) react rapidly with both O atoms and OH radicals with the formation of the corresponding
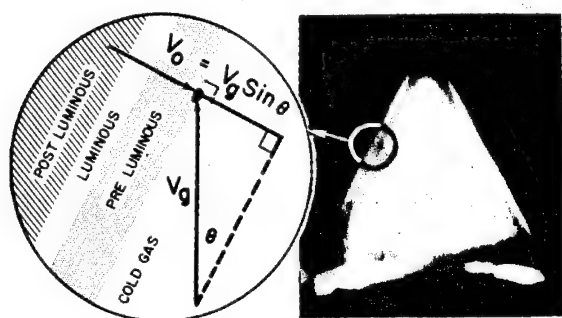
Figure 4. *Burning velocity.*

The rate at which a plane flame front advances into the unburned gas is called burning velocity. It depends principally on initial composition, temperature and pressure. At any point along a flame front the propagation velocity balances the cold gas approach velocity. For conical bunsen flames there is a simple relation between cone angle, gas velocity and burning velocity. (See above).

Table IV. *Hydrogen-halogen flame reactions*

[See table VIII, #18, 22, 23, for sources of kinetic constants]

$$
\begin{aligned}
H + X_2 &\rightleftarrows HX + X \\
X + H_2 &\rightleftarrows HX + X \\
X + X + M &\rightleftarrows X_2 + M^* \\
H + H + M &\rightleftarrows H_2 + M^* \\
H + H + M &\rightleftarrows H_2 + M^* \\
H + X + M &\rightleftarrows HX + M^*
\end{aligned}
$$
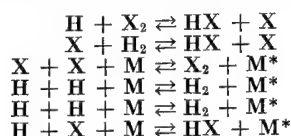
halogen atoms. In the case of Br and I the atoms are unreactive with respect to hydrogen, molecular oxygen and the common hydrocarbon fuels. The result is the substitution of a stable unreactive radical. Cl atom reactivity is sufficient so that inhibition is less pronounced and in some cases a promotion of reaction can occur (table V).

Table V. *Reactions of halogen species with oxygen atoms and hydroxyl radicals*

[See Table VIII, #18, 23, for sources of kinetic constants]

$$
\begin{aligned}
O + X_2 &\rightleftarrows OX + X^* \\
OH + X_2 &\rightleftarrows HOX + X \ (OX + HX)\dagger \\
O + HX &\rightleftarrows OH + X \ (OX + H)\dagger \\
OH + HX &\rightleftarrows H_2O + X
\end{aligned}
$$
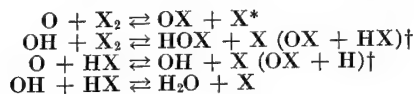
† Thermodynamically unfavorable.

Halogenated hydrocarbons are rapidly attacked under flame conditions to form halogen acids and atoms. This allows secondary inhibition reactions described above to take place (table VI).

Table VI. *Reactions of halogenated hydrocarbons with flame Radicals*

[See Table VIII, #18, 23, for sources of kinetic constants]

$$
\begin{aligned}
R\cdot X + H &\rightarrow HX + R\cdot \\
R\cdot X + O &\rightarrow OX + R\cdot
\end{aligned}
$$
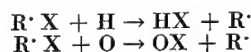
Table VII. *Groups and programs concerned with the gathering and evaluation of chemical kinetic data*

(1) **CODATA** (Committee on Data for Science and Technology). Dr. C. Schäfer, Westend Strasse 19, Frankfurt/Main, Germany. This organization was created by the International Council of Scientific Unions. A Task Group on Kinetics was charged with finding out what is being compiled. The group is headed by Dr. S. W. Benson, Stanford Research Institute, Stanford, Cal.

(2) **(U.K.)** *Office of Scientific and Technical Information.*

(3) **(USSR)** *Commission on Compilation of Rate Coefficients.* Organized February 1970 by Prof. V. N. Kondratiev to collect rate coefficients. A relevant bulletin will be published annually. Eleven Working Groups have been established: 1) Exchange, combination, and disintegration reactions of simple molecules (Chairman: A. I. Porojkova); 2) Monomolecular reactions (V. I. Vedeneev); 3) Reactions of radioactively contaminated particles (G. V. Karachevtsev); 4) Homolytic liquid-phase reactions (E. T. Denisov); 5) Heterolytic reactions (M. I. Vinnik); 6) Topochemical reactions (O. V. Krylov); 7) Reactions of solid inorganic compounds; 8) Reactions of solid organic compounds (Ya. S. Lebedev); 9) Polymerization reactions (A. A. Berlin); 10) Energy exchange processes (A. M. Tchaijkin); 11) Theoretical Group (E. E. Nikitin).

(4) **National Academy of Sciences (U.S.)** *Committee on Data for Science and Technology*, F. D. Rossini, Chairman; Ad Hoc Committee on Chemical Kinetics, S. W. Benson.

(5) **JANAF Committee on Thermodynamics and Chemical Kinetics** (formerly ICRPG Thermochemistry Working Group), J. Massey, Chairman.

(6) **Landolt-Bornstein Tabellen**, Technische Hochschule, Institut fur Technische Physik, 61 Darmstat, Germany. Dr. K.-H. Hellwege, General Editor.

(7) **Tables de Constantes Selectionnees**, 250 rue St. Jacques, Paris V^e, France, Dr. P. Khodadd, Director.

(8) **Atomic Collision Information Center**, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado, U.S.A. Dr. L. J. Kieffer, Director. Collects, evaluates and compiles data on collisions of electrons, and photons, with ions, atoms and molecules. The center is part of the U.S. National Standard Reference Data Systems. Ion-Molecule reaction rate data are included.

(9) **Atomic and Molecular Processes Information Center**, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Dr. C. F. Barnett, Director. Directory of Federally Supported Information Analysis Centers (Committee on Scientific and Technical Information, Washington, D.C., COSATI-70-1, PB 189300 (1970), No. 7.

(10) **Chemical Kinetics Information Center**, National Bureau of Standards, Washington, D. C., U.S.A. Dr. David Garvin, Director. Collects and indexes published reactions in the gaseous, liquid and solid phases, photochemistry and inelastic scattering. It is part of the U.S. National Standard Reference Data System. Prepares bibliographies for authors of reviews in the NSRDS critical review series and for the scientific public, both on request and on its own initiative. Evaluations of rate data and tables of data occasionally issued.

(11) **High Temperature Reaction Rate Data Centre**, Department of Physical Chemistry, Leeds University, Leeds, England, Dr. D. L. Baulch, Director. Evaluates rate data for gas phase reactions that are of importance at high temperature. Publishes results as "High Temperature Reaction Rate Data Reports". Nos. 1–5 issued as of 1970.

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TABLE VIII. *Sources of gas phase chemical kinetic data*

1. Anon. "Bibliography of Atomic and Molecular Processes," issued by the Atomic and Molecular Processes Information Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee. Bibliographies listing papers and reports *during stated time periods*, issued semiannually starting with the period July–December 1965. Available from the Clearinghouse for Scientific and Technical Information, Springfield, Va., USA. Hard copy $3.00, microfiche $0.65.

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5.7. Fluorocarbon Radicals

Mixed fluorocarbon-halogen molecules (F_2 and HF do not inhibit flames) are better inhibitors than would be predicted on the basis of the halogen atom concentration. This is probably associated with the stability of the fluorocarbon radicals under flame conditions. Some plausible reactions can be written, but little reliable kinetic information is available.

The principle reactions should be with hydrogen atoms. Reactions with oxygen atoms are thermodynamically favorable, but sterically difficult. CF_2 has been observed to react with molecular oxygen in a shock tube at 2000 K [21], but the elementary steps are not clear.

Thermodynamically Favorable Reactions of CF_3 and CF_2 Radicals in Flames

$$CF_3 + X + H \rightarrow HX + CF_3$$
$$CF_3 + H \rightarrow CF_2 + HF$$
$$CF_2 + H \rightarrow CF + H$$
$$CF_2 + O \rightarrow CO + 2F$$
$$CF_2 + O_2 \rightarrow CO + F_2 + O$$
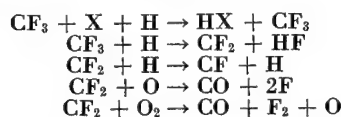
5.8. Sources of Quantitative Chemical Kinetic Data

In recent years a number of groups and individuals in this country and abroad have undertaken the compilation and evaluation of kinetic data (table VII). The results have been a substantial number of bibliographic and critical evaluations (table VIII). Two recent extensive compilations have been made by Trottman-Dickenson and Milne (Table VIII, #23), and Kondratiev (table VIII, #18). These volumes present the gas phase chemical kinetic literature in a compact form.

Extensive critical evaluations have been made by Schofield, the High Temperature Kinetics Group in Great Britain, and the National Standard Reference Group in the U. S. (table VIII, #3, 5, 15, 20). These publications offer critically evaluated kinetic data on many flame reactions. References to sources of information in this table have been given following the various reactions discussed throughout this paper.

5.9. Summary

The chemistry of flames is a complex subject, but progress has been made in the understanding of this phenomena in terms of elementary processes. The quantitative utilization of this understanding will require the accumulation and evaluation of much more information than exists at present, but a substantial start has been made.

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Discussion

Dr. R. S. Konar (Catholic University):

We face considerable difficulties in detecting and estimating HCHO quantitatively when it is found to be a product in the gas phase reactions. I would like to know in detail how Dr. Fristrom detects and estimates quantitatively formaldehyde in flames.

I wonder whether Dr. Fristrom could give us any idea about the magnitude of the rate constant of the reaction

$$H + CH_3 + M \rightarrow CH_4 + M$$

where M may be N_2 or any other inert gas.

R. M. Fristrom:

The analysis of formaldehyde offers difficulties because of its tendency to polymerize to para-formaldehyde, a six-membered ring structure. This makes it difficult to prepare standard samples for instrument calibration. Quantitative sampling requires conditions such that condensation is unimportant. Where these conditions are met, mass spectrometry and presumably other standard analytical techniques can be used.

In the case of our own flame studies, we found that formaldehyde could be reproduceably sampled using microprobe techniques with a continuous flow inlet into the mass spectrometer. Condensation, adsorption and reaction were negligible. The transfer lines were teflon coated, held at room temperature and at a pressure of the order of 10^{-1} torr. With batch sampling in glass bottles at about 1 torr condensation occurred, but sufficient formaldehyde remained after eight hours to allow identification by microwave spectroscopy. To calibrate the mass spectrometer we thermally depolymerized para-formaldehyde in a stream of argon, measured the total pressure and deduced the partial pressure of formaldehyde by difference, using the known sensitivity of the instrument to argon.

I am not aware of any direct studies of the three body recombination of methyl radical with hydrogen atoms. The reaction is probably hard to isolate from competing reactions such as $H + CH_3 \rightarrow CH_2 + H_2$, followed by $CH_2 + CH_3 \rightarrow C_2H_5$, etc. In a fuel rich (reducing) system stable products such as ethylene and ethane appear.

W. Tsang (National Bureau of Standards):

Compilations of high temperature rate data show in general large scatter and uncertainties. The fact that flame properties may be predicted on the basis of such information suggests that they are in many cases insensitive to the rate processes. Conversely, this will raise questions on the accuracy of kinetic information as extracted from flame properties.

R. M. Fristrom:

This is a question of which reactions are under discussion and which reactions are relevant. Recent critical compilations such as those of the High Temperature Reaction Kinetic program at the University of Leeds, England, and others mentioned in Table VII list a number of reactions where agreement among recent reliable experimental studies lies within a factor of two. On the other hand many or most reactions are still in doubt by several orders of magnitude. The situation is improving. If one is interested in an overall flame property such as burning velocity or a single parameter such as engine thrust, studies have shown that these processes are controlled by a few (<10) of the hundreds of reactions which can be written. If the critical reactions are known with precision (and these are often well studied for just this reason), then it makes little difference whether the parallel reactions are in doubt. If one is interested in trace species or detailed processes, however, the situation is very clouded.

The reverse side of this coin is the use of flame studies to deduce kinetic parameters.

Here, if one can isolate a flame process which depends principally on a single reaction, then flames offer a good media for studying high temperature reactions (ref. 2). Otherwise, the situation is hopeless. It should be pointed out that this is generally true of kinetic systems.

Carbon Formation in Premixed Flames

K. H. Homann

Institut für Physikalische Chemie der Universität Göttingen, Göttingen, West Germany

In this paper a survey is given on the processes leading to the formation of solid soot particles in premixed flames. Like most combustion products carbon formation is not exclusively determined by flame chemistry but is also dependent on transport processes. A local increase in the overall C/O ratio in the burning zone which is connected to the back diffusion of hydrogen and hydrogen atoms can reinforce carbon formation. This gives rise to the different types of carbon appearance in burner flames. It is shown that the C/O ratio at the site of carbon formation can be very different from that of the initial mixture.

For the formation of soot particles the presence of both highly unsaturated hydrocarbons and hydrocarbon radicals is necessary. The process of particle growth which cannot be described by equilibrium condensation theory shows two distinct phases: (1) A first phase of rapid growth which is due to the addition of higher unsaturated hydrocarbons to a particle surface with radical character. During this phase the number density of particles decreases while the individual particles retain their almost spherical shape. This is followed by (2) a phase of slow growth governed by the heterogeneous decomposition of a variety of unsaturated hydrocarbons on the particle surface which has lost most of its radical-like properties.

Key words: Acetylene-oxygen flame; benzene flames; bunsen flames; carbon limit; concentration profiles; cyanogen-oxygen flame; flame front curvature; hydrocarbon radicals; hydrogen diffusion; carbon formation; oxidation reactions; particle size; transport processes.

1. Introduction

Particles of solid carbon, or rather soot particles, are among those products of combustion processes which have been studied most intensely and under many different aspects. A large number of facts about carbon formation and soot properties has been obtained since M. Faraday's famous lecture, "The Chemical History of a Candle" [1].[1] In this lecture he pointed out that carbon particles are set free by the decomposition of the vapor of the wax, that they rise up heated and glowing and are totally burned when they come into contact with the surrounding air. These three phases: formation, radiation, and combustion of carbon particles are still subjects of intense studies. Interest in them has risen to the same extent as the industrial and ecological importance of carbon formation has grown in the last few decades. The greatest efforts have focussed on the control of carbon formation and combustion, ranging from zero yield to the largest possible production of soot under given conditions. These studies are complicated by the fact that carbon formation is very sensitive to many kinds of inhomogeneities that can be present in a combustion system, such as those of composition, temperature, flow conditions, walls etc. In the following we wish to restrict ourselves to the formation of carbon in premixed laminar flames of various fuels, mostly hydrocarbons.

2. Appearance of Soot-Forming Burner Flames

The sensitivity of carbon formation to inhomogeneities in the system gives rise to different types of sooting flames that can be observed on Bunsen or nozzle burners: From the classification of these flames as given by Behrens [2] (1951) and by Street and Thomas [3] (1955) two groups shall be mentioned:

(1) The acetylene type flame where carbon appears equally distributed above the whole flame cone. (See fig. 1).
(2) Other types of flames, where carbon formation is seen only at the tip of the flame cone, either close to the flame front (e.g. benzene) or a short distance above (e.g. cyclohexane). (See figs. 2a b.)

In most hydrocarbon-air or hydrocarbon-oxygen flames, except for very light fuels such as acetylene and ethylene, carbon appears under normal conditions in the way mentioned under (2).

The limits of carbon formation, i.e., the ratios of carbon to oxygen in the unburnt gas at which soot formation is just observed, are also based to a large extent on flames of type (2). These limits were measured by Street and Thomas [3].

However, the limits and the amount of carbon formation for a certain fuel-oxidizer pair are determined not only by the mixture ratio. Also the flow conditions at a given temperature and pressure can

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[1] Figures in brackets indicate the literature references at the end of this paper.

FIGURE 1. *Acetylene type.*

markedly influence the carbon formation. Using a nozzle burner it can be demonstrated that a small variation in flow which results in a change of the shape of the flame can reinforce or weaken carbon formation. A normally cone shaped benzene-air flame forming carbon at its tip can be made to switch to a nonluminous flame forming a button-shaped flame front without alteration of the mixture ratio or the through-put of gas [4]. Compared to the cone shaped flame this flame lacks a strong curvature of its combustion zone since it does not have a sharp tip.

Other examples of reinforced carbon formation above strongly convex portions of the flame front (concave relative to direction of gas flow) are the appearance of carbon streaks above the ridges of disturbed flames of the polyhedral type and above the many small tips of cellular flames [5].

The influence of flame front curvature on carbon formation is not restricted to stationary flames. Gaydon describes a Bunsen flame burning without carbon formation but near the limit thereof. If one now varies the flow velocity periodically then the carbon streaks are emitted from the tip in phase with the variation of the flow which also results in a variation of the flame curvature at the tip [6]. In turbulent flames there are turbulence balls with rapidly varying curvatures of the local flame front which also will influence carbon formation in the same sense.

3. Influence of Transport Processes

What is the reason for such localized appearance of carbon formation in many flames? The examples

FIGURE 3. *C/O ratio for an n-heptane-air flame burning at the limit of carbon formation as function of the height above the burner, measured along the axis of the flame cone.*

given above seem to indicate that the same reasons that give rise to polyhedral flames are also related to the localization of carbon formation. This would mean that the mixtures entering the various parts of the flame front are not the same and are different from the gas mixture fed to the burner. Accordingly the burning conditions are not the same.

It has been shown by Jost and co-workers that the C/O ratios at the tip of a Bunsen cone and above the ridges of polyhedral flames are larger than those above other parts of the flame [7]. More recently, measurements along these lines have been carried out on an n-heptane-air-flame burning just slightly below the limit of carbon formation [8]. It was a polyhedral flame of 27 mm height having 9 ridges. Figure 3 shows the variation of the C/O and C/H ratios along the axis of the flame. There is a steady increase of the C/O ratio towards the tip of the flame, becoming rather pronounced near the reaction zone. This is accompanied by a decrease in the C/H ratio. Behind the flame front these ratios tend towards their original value. In still richer mixtures this increase in C/O ratio develops so far

FIGURE 2. a. *Benzene type;* b. *Cyclohexane type.*
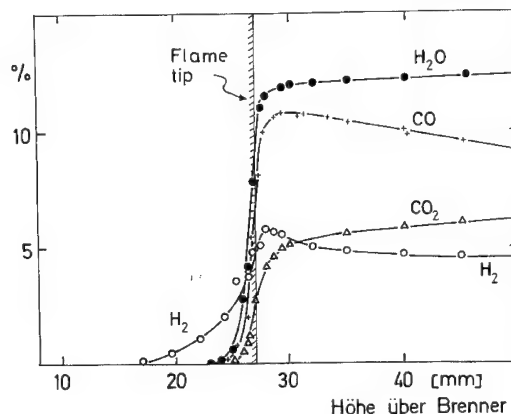
FIGURE 4. *Concentration profiles along the axis of the flame cone of the flame from figure 3.*

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that the limit of flamability is surpassed and the flame front breaks up at the tip.

A more detailed picture is given by the concentration profiles in figure 4. It is seen that the decrease in the C/H ratio is mainly due to the comparatively large amount of hydrogen diffusing back into the unburnt gas. A similar situation is found when measuring concentration profiles through ridges of the flame front. From concentration measurements on flat hydrocarbon-oxygen flames it was known that hydrogen diffuses farthest back into the unburnt gas [9, 10]. However, this concentration of hydrogen cannot be explained simply by diffusion back from the tip of the flame.

Because of the complexity of the interdependence of transport processes and chemical reaction in a Bunsen flame only a qualitative and necessarily incomplete picture can be given here of the phenomena that cause these variations in mixture ratios, see also [11]. Let us first consider the situation in an ideally cone shaped flame front, a cross section of a part of which is shown in figure 5. The straight lines
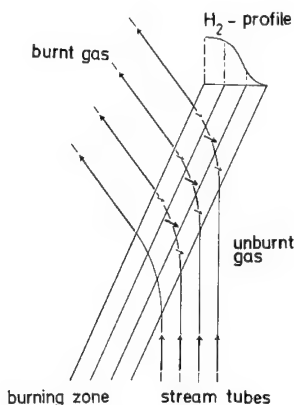
FIGURE 5. *Diffusion of hydrogen in the burning zone of an ideally cone-shaped hydrocarbon-air flame.*

indicating an extended flame front shall represent the lines of constant hydrogen concentration, a profile of which is represented schematically at the upper ends of the lines. The stream tubes of the gas stream go through the burning zone as indicated. Hydrogen diffuses back against the gas stream along its concentration gradient. Thus, hydrogen diffuses not only out of one volume element—arbitrarily defined by two lines of constant H_2 concentration and two stream tube boundaries—into the element directly upstream from it, but also into its neighboring volume element at the side towards the tip of the flame. But through this there cannot be an appreciable enrichment of H_2 towards the tip, since the same amount of hydrogen is diffusing into the volume element from its other neighbor at the side towards the base of flame.

However, this situation cannot be stationary if a slight increase in hydrogen concentration in one volume element decreases the local burning velocity. This is just what happens in mixtures of hydro-

carbons and air near the limit of carbon formation. As a consequence the flame front curves. If the lines of constant hydrogen concentration would curve in the same way there would be a net flow of hydrogen towards the tip which again would cause a further curvature of the flame front leading to an unstable situation. Since there *is* a stable flame, the lines of constant H_2 concentration will assume the form indicated by the dotted lines of figure 6. This again
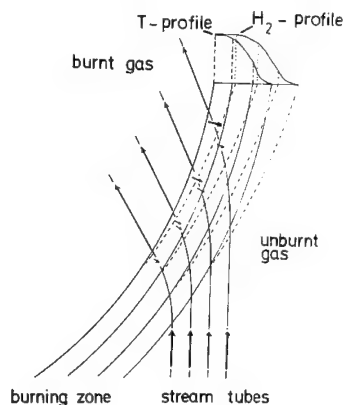
FIGURE 6. *Diffusion of hydrogen in a curved flame front of a hydrocarbon-air flame.*

balances the transport of hydrogen in and out of the imaginary volume elements, but causes an increasing H_2 concentration towards the tip when measured along the axis of the flame.

Since the pressure in the flame does not change, this diffusion of hydrogen towards the tip and the axis must be balanced by a diffusion of unburnt gas in the opposite direction. If the diffusion coefficients of fuel and oxygen in the mixture are sufficiently different as in the case of n-heptane-oxygen, oxygen diffuses faster towards the flame zone and causes an increase in the C/O-ratio measured along the flame axis. Since this increase is strongest towards the tip of the flame it is here where the carbon formation sets in. That the back diffusion of hydrogen is related to the appearance of carbon can be shown in a simple experiment.

It is possible to eliminate that part of the hydrogen diffusion which is caused by molecular hydrogen by adding to the unburnt mixture a certain amount of hydrogen so that the mole fraction of it in the unburnt gas becomes nearly equal to that in the burnt gas. The appearance of such a flame when sooting is very similar to that of an acetylene type flame: carbon luminosity appears above the whole flame cone; furthermore, the slightly bent flame front straightens out and resembles more that of an ideal cone. It is to be noted, however, that the carbon luminosity is still strongest at the tip [4]. These few examples show that transport processes, especially the back diffusion of hydrogen from parts of the burning zone, have a strong influence on the carbon formation. The appearance of carbon at regions of high curvature of the flame front, however, cannot be attributed to a single effect. For a more complete

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picture the diffusion of hydrogen atoms, and other light radicals, must be taken into account. Furthermore, the steady rise of temperature may cause pyrolysis ahead of the visible burning zone. The heating of the unburnt gas would be particularly effective within the cavity of a convex portion of the flame front.

Thus, in most cases carbon formation is not only controlled by the flame chemistry but also by the burning conditions. At the local site of carbon formation the mixture in terms of the C/O and C/H ratios may be very much different from that in the fresh gas. It shows that one should be careful in using limiting C/O ratios measured in the unburnt gas for a discussion of the chemistry or even mechanistic aspects of carbon formation. This does, however, not diminish the great practical value of these measured figures.

4. Theoretical and Practical Carbon Limits

The critical C/O ratio in the unburnt gas at which carbon appears in practical flames ranges from 0.4 for heavy fuels to about 0.9 for light fuels such as acetylene, as measured by Street and Thomas [3] and others. For solid carbon in thermodynamic equilibrium with the flame gases, this ratio should be fairly independent of the fuel and should have a value very close to unity, changing somewhat with the temperature, e.g. [12]. The measurements of the variation of the C/O ratio of the unburnt gas along the axis of a sooting Bunsen flame shows that this ratio could increase quite steeply. This raises the question whether it might reach the theoretical value of about unity in the actual combustion zone at the tip where the carbon is formed. Measurements on a flame burning at 1 atm could not be carried out directly in the flame front because of interference of the probe with the narrow combustion zone. However, concentration measurements in the combustion zone of flat flames at lower pressure showed that the ratio does not reach its theoretical value at the point where sooting begins [10, 13]. The practical carbon limits in flat flames are on the average only 10-13 percent higher than those in Bunsen flames [14]. If the fuel-oxidizer mixture is burned in a well-stirred reactor, the carbon limits are 10-20 percent higher than in conical flames [15].

These limits of carbon formation and more detailed measurements of the composition of sooting hydrocarbon flames show that the process of carbon formation takes place under non-equilibrium conditions. It is, therefore, intrinsically different from the condensation of a normal vapor where the liquid droplets represent an equilibrium state [16]. There is no critical size of carbon particles above which the rate of growth (as in condensation) is greater than the rate of vaporization and which could be correlated with a certain degree of supersaturation of carbon vapor. The only flame known in which carbon formation seems to take place almost under equilib-

rium conditions is the very hot cyanogen-oxygen flame [17].

5. Chemistry of Carbon Formation

Since carbon formation in hydrocarbon flames is recognized to be governed by chemical kinetics rather than through thermodynamic equilibrium one
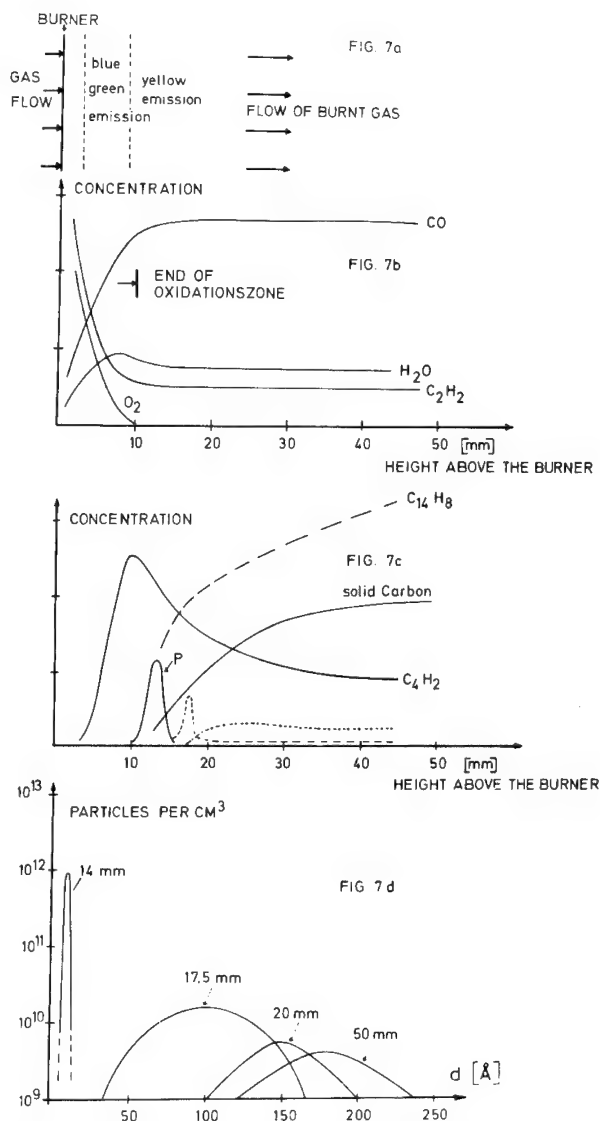
FIGURE 7. *Particle history in a flat C_2H_2-O_2 flame burning at 20 mm Hg, C_2H_2/O_2 approx. 1.4.*

(a,b) Scheme of the flame and schematic representation of the concentration profiles of main components. The mole fractions at a distance of 40 mm above the burner are approximately: CO: 0.56, H_2O: 0.05, C_2H_2: 0.12. Curves are not to scale among each other.
(c) Schematic representation of various products. The mole fractions at 40 mm above the burner are approximately: C_4H_2: 0.016, $C_{14}H_8$: $6 \cdot 10^{-6}$; solid carbon: 0.25 percent by weight. Precursors of carbon particles $p \approx 10^{-5}$ at 14 mm; ••••• represents the change of number density of carbon particles with diameters around 100 Å; –•–•–•– represents the change in number density of carbon particles with 200 Å diameter.
(d) Distribution functions: The number of particles/cm³ in a certain diameter interval plotted against the diameter for various heights above the burner. The height is given as parameter. The function at 14 mm represents the precursors p. The number of acetylene molecules/cm³ which is transferred into carbon is ca. $4 \cdot 10^{14}$ at burned gas density.

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must ask: What happens to hydrocarbon molecules in flames until their carbon atoms appear in solid particles. Some insight into the various steps of that process has been obtained from investigations of flat hydrocarbon flames burning at reduced pressure. The use of reduced pressure was necessary to obtain sufficiently extended reaction zones [13, 18].

In order to follow the formation of solid particles the following questions should be considered:

(1) What are the main products formed in the oxidation zone of the flame?
(2) Which intermediates are formed during the combustion of the fuel?
(3) Which higher carbon containing species are formed in the reaction zone and what are to be considered the precursors of carbon particles?
(4) How do the carbon particles grow?
(5) How does the total amount of carbon increase in the particles and what are their properties in the various stages of their growth?

As an example, some experimental answers to these questions obtained from acetylene-oxygen flames burning at pressures around 20 mm Hg will be discussed (see fig. 7).

The main reaction products are CO, H_2O, CO_2, H_2 and C_2H_2 (fig. 7b). Another group of products, the concentrations of which show maxima at the end of the oxidation zone, are polyacetylenes ($C_{2n}H_2$). In the burnt gas their concentrations remain practically constant at this pressure. Together with C_2H_2 and H_2 they form a kind of equilibrium. A very similar situation arises in flames of other hydrocarbons. In figure 7c concentration profiles of polyacetylenes are represented by that of C_4H_2, their maximum concentration decrease rapidly with increasing numbers of carbon atoms in the chain. In the oxidation zone which ends with the consumption of oxygen a variety of other hydrocarbons are found, such as propylene, methylacetylene, dimethylacetylene, vinylacetylene, benzene, methane and others. They all reach a concentration maximum inside the oxidation zone and have practically disappeared when oxygen is consumed.

In addition to the stable components mentioned several radicals such as C_2H_3, C_2H, C_2, CH, H, O, OH etc. have been analyzed in the reaction zone of an acetylene-oxygen flame [10, 13]. The large number of various positive and negative hydrocarbon ions that can appear in hydrocarbon flames may be seen from measurements of Sugden and co-workers [19].

Another characteristic group of hydrocarbons formed in that flame is the polycyclic aromatic hydrocarbons such as naphtalene, phenanthrene, pyrene, 3,4 benz-pyrene, coronene and related species. The concentration profile of one of them ($C_{14}H_8$) is shown in figure 7c. These species start to appear at the end of the oxidation zone and keep steadily increasing in concentration in the burnt gas, even in that region where carbon formation has become immeasurably slow under low pressure conditions.

Still another group of hydrocarbons was detected in the gas phase (P in figure 7c). They have molecular weights between about 150 and 550 (550 was the limit of the mass range of the analyzing mass spectrometer). In contrast to the aromatics mentioned above their concentration shows a maximum between 12 and 14 mm above the burner and they disappear again within the zone where the carbon particles grow [20]. The number of carbon atoms in them ranges from about 15 to above 40. Their hydrogen content is larger than that for condensed aromatic species of the same number of carbon atoms. Although they have not yet been identified individually, many of them seem to contain side chains. With increasing height in the flame the relative concentration maximum within this group is shifted to higher molecular masses, while their absolute concentration decreases steadily. They are considered to be important intermediates for the formation of solid particles.

The individual concentration of the P type species while further growing become too low for a direct analysis until the first small carbon particles, 20 to 30 Å in diameter, can be perceived by aid of electron microscopy a few mm further in the burnt gas. Sampling of carbon particles from various heights in the flame gave the following results:

(1) The size of the particles increases continuously up to about 50 mm above the burner.
(2) The number of particles decreases in that range.
(3) The total amount of solid carbon increases during this process.
(4) The agglomeration of individual particles into the well-known grape or bead-like clusters occurs in a later stage.

At greater heights in the flame no marked change in particle size and total amount of carbon was observed. This means that a continued formation of carbon in the burnt gas (which would have to be measured in flames burning at higher pressure) must be much slower than the process described. The distribution functions of particle size at different heights in the flame show that the number of particles with diameter less than 100 Å has become very small even at 20 mm above the burner. This means that the rate at which new small particles are formed at this height of the flame is negligibly small. From figure 7d one can see that the intermediate hydrocarbons (P) which are considered here as "carbon particles" of 8 to 10 Å diameter fit quite well into the scheme.

It is not only the size of the particles that changes during this phase of rapid growth but also their chemical and physical properties. Their H/C ratio, for example, steadily decreases towards greater heights above the burner. E.S.R. signals obtained from carbon particles sampled at various heights show a continuous and rather strong decrease from "young" to "old" carbon particles. When rapidly cooling a flame gas sample containing carbon

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particles a large numbers of higher hydrocarbons will condense on the particles. They can be evaporated again when the carbon is heated under vacuum. In agreement with the direct gas phase analysis there are mainly aromatics with the carbon particles from greater heights in the flame while hydrocarbons of type P are collected with the "young" particles [21].

6. Discussion of the Process of Carbon Formation from Aliphatic Fuels

What can be said about the essential steps of the process of carbon formation on the basis of these experimental results? The initiation of carbon formation in premixed flames under the conditions discussed is definitely related to the chemical reactions in the burning zone where the oxidation process gives rise to various types of radicals in rather high concentrations. This is in contrast to the mainly pyrolytic decomposition of the fuel and subsequent particle formation in diffusion flames.

Both the production of hydrocarbon radicals and of highly unsaturated hydrocarbon molecules is essential for the initiating steps of very complicated sequences of reactions which finally lead to the formation of solid particles.

The unsaturated hydrocarbons which are formed as intermediates or final products in the combustion of different lower aliphatic fuels are essentially the same. They differ only in concentration depending mainly on the nature of the fuel molecules. Very often their relative concentrations are almost identical if the flame temperatures do not differ too much.

The main unsaturated species formed in the oxidation zone are acetylene, polyacetylenes, methylacetylene, ethylene, propene, vinylacetylene, and butadiene. Of these, however, mainly acetylene and polyacetylenes are still present at the end of the oxidation zone where carbon formation begins. The other hydrocarbons disappear again at an earlier stage in the oxidation zone. In view of this situation we shall limit our discussion of the first steps leading to carbon formation to those in which acetylene and polyacetylenes are involved.

That the presence of radicals which are generated by the oxidation reaction is necessary for a rapid formation of carbon can be clearly seen from the situation in the burnt gas. Here, acetylene, polyacetylenes and polycyclic aromatics are still present in appreciable concentrations but the formation of new particles or the increase of soot has apparently become very slow. Thus, carbon formation is only rapid in the vicinity of the radical-rich oxidation zone but it slows down with decreasing concentration of small hydrocarbon radicals.

In premixed flames hydrocarbon radicals are mainly formed by reactions of hydrocarbons with active species such as O, OH, and hydrogen atoms. In connection with carbon formation we will only consider those with acetylene and polyacetylenes for the same reasons as above.

The study of the reaction of O-atoms with acetylene over a temperature range of a few hundred degrees shows that the main reaction proceeds via [22]

$$O + C_2H_2 \rightarrow CH_2 + CO$$
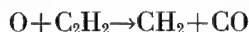
$$(k \approx 10^{13} e^{-2800/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}).$$

H atoms and OH radicals react with acetylene to give

$$H + C_2H_2 \rightarrow C_2H_3 \text{ [23]}$$

and

$$OH + C_2H_2 \rightarrow CO + CH_3, \text{ respectively [24]}.$$
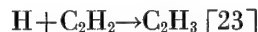
These reactions give rise to the radicals CH_2, C_2H_3 and CH_3. Furthermore, C_2H radicals, the source of which is not yet certain, have been observed in acetylene flames.

Primary products of the corresponding reactions of diacetylene are not known. It is not unreasonable, however, to assume that CO is also one of the primary products which makes probable the formation of C_3H_2 and C_3H_3 for the reaction with O and OH, respectively. Reaction with H-atoms will certainly involve the formation of C_4H_3. The fate of these radicals will be oxidation in flames rich enough in oxygen to prevent carbon formation. In sufficiently fuel rich flames the concentration of acetylene and polyacetylenes are high enough so that addition reactions of these radicals to the acetylenes are faster than the oxidation reactions.

In an excess of acetylene a consecutive reaction of the CH_2 radical gives

$$CH_2 \cdot + C_2H_2 \rightarrow C_3H_4 \cdot$$

which at lower temperatures will stabilize to methylacetylene. In analogy to this reaction, $CH_2 \cdot + C_4H_2 \rightarrow C_5H_4 \cdot$ is probable. In a similar way radicals such as CH_3, C_2H_3, $C_2H \cdot$ can add to acetylenic hydrocarbons and produce higher hydrocarbon radicals. As pointed out by Porter [25] the presence of double and triple bonds is very important because it enables these particles to maintain their radical character during further addition of small highly unsaturated hydrocarbons. The radical character is to a large extent still present in "young" carbon particles.

The addition of small radicals to acetylene and to terminal carbon atoms of polyacetylenes causes the formation of diacetylene and higher polyacetylenes, respectively. Measurements of polyacetylene concentrations in flames under different conditions suggest that the single addition reactions are fairly well equilibrated. This leads to a quasi-equilibrium between acetylene, the polyacetylenes, and hydrogen as long as radicals are present.

Addition of a radical to a nonterminal carbon atom of a polyacetylene, however, does not easily lead to a stable branched molecule so that by further addition of acetylene and polyacetylenes a highly branched radical can be formed. For this mechanism, growing biradicals such as CH_2 or C_3H_2 are much more effective than normal radicals. The larger those
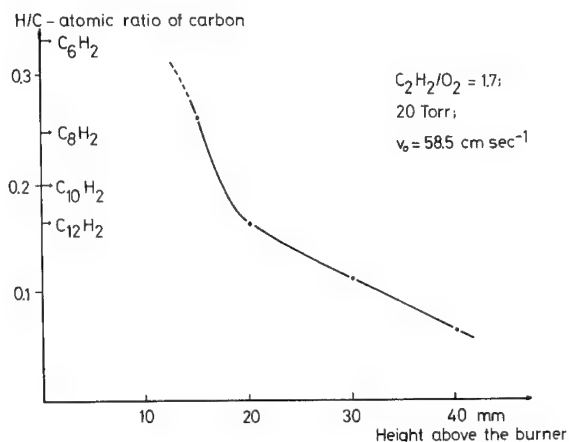
Figure 8. *H/C-ratio in the carbon particles of a C_2H_2-O_2 flame with $C_2H_2/O_2 = 1.7$ as a function of the distance above the burner.*

($p = 20$ mm Hg, $v_0 = 58.5$ cm/s)

radicals grow the more easily can they make internal additions i.e. ring closures while the whole particle retains its radical character. Through recombination of two such radicals or through "internal recombination" (ring closure of a branched biradical with loss of the radical character) hydrocarbons of the type P and also the much more stable polynuclear aromatic species can be formed. From the concentration behavior of the aromatics in the flame and also from their known comparatively high thermal stability it must be assumed that they are byproducts in the process of carbon formation rather than important intermediates [26, 27].

These large branched and ring-containing hydrocarbon radicals add predominantly acetylene and diacetylene first without losing hydrogen. This is indicated by the atomic H/C-ratio in the first carbon particles (fig. 8). During the formation of carbon both the large hydrocarbon molecules and the small soot particles between which there is a continuous transition decrease in number concentration while the total amount of soot increases. Apparently two things happen: (1) small carbon particles (and also large hydrocarbon radicals) which come together will coalesce; (2) these particles continue to add hydrocarbons from the gas phase. In a later phase of growth the carbon particles—by a kind of internal tempering process—give off hydrogen and loose much of their radical character. This prevents a further rapid growth just by addition of hydrocarbon molecules. As a consequence the increase in the amount of carbon slows down and continues only by heterogeneous decomposition of hydrocarbons on the surface of the carbon particles. This, however, is a slow process as compared to the one described.

7. Carbon Formation from Aromatic Fuels

In flames of benzene and related aromatic fuels the situation is different in so far as even at the beginning of the process rather large hydrocarbon molecules are present as "building bricks" for carbon particles. This increases the rate of forming higher hydrocarbons relative to the rate of oxidation. It causes the zone where the small soot particles begin to grow to overlap more with the oxidation zone of the flame. Thus, in addition to the presence of large hydrocarbon molecules from the beginning, carbon formation is reinforced here because it starts even in a flame zone where the concentration of small radicals is relatively higher than in the zones where particle formation starts in flames of lower aliphatic fuels [26].

In zones of rapid particle growth in a benzene flame similar polycyclic hydrocarbons of type P, as in acetylene flames, are found. Again condensed aromatics that are formed behave like comparatively inert byproducts in the process of carbon formation.

Although the concentration of higher hydrocarbons and hydrocarbon radicals may be quantitatively different in the carbon forming zones of flames of different fuels, qualitatively they are similar, even for fuels such as alcohols.

The examples discussed in this paper naturally cover only a part of the problem of the chemistry of carbon formation. Even for the phase of formation of carbon there are many aspects that could not be discussed here, such as carbon formation in diffusion flames, the influence of additives and of electrical fields on the carbon content of flames, to mention only a few. Many details of carbon formation not mentioned here are contained in recent review articles by Gaydon and Wolfhard [6], Palmer and Cullis [28], Thomas [29], and Homann [4, 21].

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Discussion

Henry A. Hill (Riverside Research Laboratory, Inc.):

An initial comment related the finding of the cyclic carcinogens (benzpyrenes) in vapors formed by fats dropping onto hot wood or coal carbons in the charcoal broiling of foods.

The second comment asked the effect of a solid phase of red hot carbon in the burning zone on carbon formation and the backward diffusion of hydrogen. From this the next question tied together Dr. Wall's question about the presence of a 1600 molecular weight fragment of polymer in vapor phase in flame to the presence of added mechanically propelled (not vaporized) carbon particles into the flame as nuclei for growth or as fuel for combustion. What happens to added carbon particles in the zone of hydrogen diffusion?

K. H. Homann:

As far as I know there is no direct experimental information on the influence of artificially added carbon particles on the formation of new particles. According to the experiments on burning carbon particles one may guess that most of the carbon particles will be oxidized in the burnt gas of the flame if its mixture ratio is below the limit of carbon formation. If the flame forms soot by itself injected carbon particles will not influence the generation of new small particles but will grow by heterogeneous decomposition of hydrocarbons on their surfaces.

C. F. Cullis (The City University, London):

The kinetic parameters of the reaction:

$$C_2H\cdot + C_2H_2 \rightarrow C_4H_2 + H \qquad (1)$$
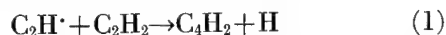
which has been shown to be fast [1] are at present being measured at the City University, where, by the use of acetylene-d_2, it is possible to distinguish reaction (1) from the hydrogen-transfer reaction:

$$C_2H + C_2H_2 \rightarrow C_2H_2 + C_2H. \qquad (2)$$
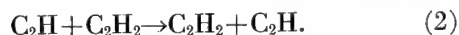
The widespread occurrence of reaction (1) during the formation of carbon from acetylene also receives indirect support, however, from evidence that diacetylene (a product of reaction (1)) is an important intermediate in the carbon-forming process. Thus, although vinylacetylene is under a wide range of conditions the principal primary product of the breakdown of acetylene [2–6], kinetic and analytical studies of the pyrolysis of the former compound [7], together with isotopic tracer investigations [8], suggest that the dimer is not an important intermediate in the formation of carbon from acetylene. On the other hand, diacetylene, which produces carbon much faster than does acetylene under comparable conditions [9–10] almost certainly plays a much more prominent role.

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K. H. Homann:

Preliminary measurements on the reaction

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \qquad (1)$$
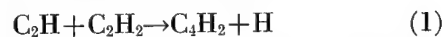
at a temperature of about 500 K have rendered a $k_1 \approx 2 \cdot 10^{12}$ cm^3/mol s [1]. This figure can be compared with a rough estimate from measurements of the C_4H_2 profile in an C_2H_2–O_2 flame and the C_2H concentration as estimated in such a flame [2]. If it is assumed that at the maximum of the C_4H_2

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profile the rate of formation of C_4H_2 by reaction (1) equals the rate of consumption through O atoms and OH radicals a k_1 of (3 to 4)$\cdot 10^{12}$ cm^3/mol s at a temperature of about 1900 K is obtained. This estimate also implies the assumption that according to measurements of Niki [3] C_4H_2 reacts 6 to 8 times faster with O atoms (and also with OH?) than does C_2H_2. Although this is a very rough estimate it shows at least agreement within much less than an order of magnitude. There is evidence, however, that also the reaction $C_2H_3 + C_2H_2$ can contribute to the formation of C_4H_2 in flames.

A still unsolved problem is the source for C_2H in C_2H_2–O_2 flames. All experiments on reactions with acetylene and active particles seem to indicate that the source must be a reaction with an appreciable activation energy that can only be observed at higher temperatures. At lower temperatures other reactions not leading to C_4H_2 are much faster.

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H. B. Palmer (Pennsylvania State University):

The observation that flame inhibitors frequently enhance carbon formation can be qualitatively understood by noting that in any hydrocarbon flame there will be competition between oxidation reactions and "cracking"-type reactions. The latter are the steps that may ultimately produce carbon. Anything that slows the oxidation is apt to enhance the relative significance of cracking. Work by Roger Millikan several years ago showed that the critical question in carbon formation probably is the competition between oxidation of some intermediate by OH and the reaction of that intermediate with other species that can lead to carbon formation. But in flame propagation, we know that OH also plays an important part in carrying chains, and inhibitors may function by removing OH. Thus, in general, inhibition can be expected to increase the carbon-forming tendency of a flame, because of the significance of OH both in flame propagation and in the prevention of sooting.

K. H. Homann:

The point of view that carbon formation or no carbon formation in premixed flames is the result of a competition between oxidation reactions in which OH and O atoms play a role and "cracking"-type reactions is in principal correct—although these "cracking"-type reactions can be quite different from those known to occur in cracking or in pyrolysis. Considering the role of inhibitors in influencing the burning velocity by removing OH radicals or other active species and increasing the carbon forming tendency one has to differentiate. It depends very much on the conditions of burning, on the nature of the fuel, on the temperature where carbon formation begins and on other parameters whether the inhibitory effect is paralleled by an increased carbon formation. In oxyacetylene flames, for example, a relatively large concentration of OH in the oxidation zone before the temperature reaches its maximum leads to formation of CO_2 and H_2O in excess of those concentrations which correspond to the equilibrium at the final flame temperature. Thus, too much oxygen is bound in products other than CO and is lost for the prevention of carbon formation. An inhibitor which serves for suppressing the OH concentration in lower temperature zones of the flame and forces the combustion to take place at a higher temperature on the average will prevent this. In this way carbon formation will be reduced and not enhanced.

Donald Aldrich (Massachusetts Institute of Technology):

You implied that carbon formation in premixed flames follows a different mechanism from that in diffusion flames. This, of course, is understandable if a different fuel is used in the two types of flames, but it is not clear if the same fuel is used in both cases. There are obvious physical differences, but what is the difference in the chemical mechanism of carbon formation in premixed and turbulent flames if one considers this formation to result from the same chemical species in both cases?

K. H. Homann:

The main difference in the "mechanisms" of carbon formation in diffusion flames and premixed flames lies in the early stages of carbon formation. In premixed flames two stages of carbon formation can be distinguished. The first and faster one is strongly coupled to the oxidation reactions and the small hydrocarbon radicals formed herein. The second consists mainly in heterogeneous decomposition of hydrocarbons on the surface of soot particles. This second process can in principle also occur in diffusion flames. If carbon is formed in the absence of oxygen which can be the case in diffusion flames the precursors of carbon particles must be products from pyrolytic reactions of the fuel. Pyrolytic reactions, however, are quite different from those reactions in the oxidation zone of premixed flames leading to higher unsaturated hydrocarbons. A phase of rapid particle formation comparable to that directly behind the oxidation zone of premixed flames which is due to a large concentration of highly unsaturated hydrocarbons and a relative large concentration of hydrocarbon radicals has not been found with carbon formation in the absence of oxygen.

In turbulent flames, of course, both "mechanisms" are operative depending on the degree of premixing and on the condition of combustion.

Fluorocarbon Combustion, Fluorine Supported Combustion Kinetics?

Edward A. Fletcher

Department of Mechanical Engineering, University of Minnesota, Minneapolis, Minn. 55455

Some interesting characteristics of the combustion behavior of freons, and fluorocarbons are presented. The flame speeds and spontaneous ignition limits of chlorine burning in fluorine are easily described by simple models using well characterized kinetics. The flame speeds of CF_3Cl-F_2 and CF_3Br-F_2 mixtures can be discussed in terms of simple thermal theories. The striking differences in the combustion behavior of homologous fluorocarbons are shown to depend on big differences in the rates at which the fuel molecules are initially attacked by the competitive combustion reactions, but the kinetics are not yet understood.

Key words: Chlorine; combustion; explosion limits; flame speed; fluorine; fluorocarbons; freons; ignition limits; kinetics.

1. Introduction

When Dr. Wall invited me to talk about combustion kinetics at this meeting, I was honored and delighted to accept. I had planned to talk about combustion phenomena using the usual textbook approaches to the kinetics, i.e., global kinetics, and to illustrate some of the points from our own in-progress work with fluorine supported and fluorocarbon combustion studies. When I finally got the printed program and book of abstracts I realized to my dismay that Sidney Benson and Bob Fristrom would probably scoop everything that I had planned to say about kinetics in a general way. Besides, I felt a little like the victim of the Johnstown flood who agreed to give, in heaven, a seminar on his experiences, only to discover that Noah was to be in the audience. Nevertheless, despite the hazards, my subject still will be as announced in the program.

Flames have been called the poorest of all possible systems in which one can do kinetic studies[1] [1]. Whether that statement is true or not depends on what one means by kinetic studies. Although the rates and mechanisms of chemical reactions are extremely important in determining how pyrolizing or burning systems behave, kineticists and combustion men are rarely talking about the same thing when they use the same words. Sometimes even a given individual uses the same words to mean different things, depending on whether he's talking as a kineticist or a combustion man [2, 3]. On rare

occasions, realistic kinetics has been applied to compute flame structures and speeds [5, 6] and ignition limits [7], but the techniques one has to resort to are not very useful, whereas the most useful models use techniques that are repugnant to the kineticist. This uncomfortable state of affairs exists because many models that are, at best, heuristic work quite well, and in science and technology we frequently pragmatise: If it works it must be right.

Thus, any number of flame speed "theories" that, in their fashion, work, have been proposed [8, 9, 10]. Most of them include an energy equation which contains a "global" reaction rate term. The rate is given by a rate constant which varies exponentially with the temperature; the variation depends on an "activation energy". Having written the equation, the theoretician devotes his effort to solving it, along with momentum and continuity equations, revealing much ingenuity and sometimes brilliance, having forgotten, in the meantime, that the exponential term that is causing his difficulties is not real anyway. To a kineticist, an activation energy has, he hopes, a real, physical significance related to the mechanism of a specific elementary reaction. In combustion processes, it's just a device that gives you a term that looks like an elementary reaction rate and can sometimes fool you into believing that you have gotten insights when, in fact, you haven't. The combustion man hopes it will work, i.e., have applications; it frequently does, because the "rate constants" of complicated reactions can often be represented as products of the rate constants of

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[1] Figures in brackets indicate the literature references at the end of this paper.

elementary reactions.[2] The fact is interpreted to mean that the kinetics and mechanism of the combustion process are understood, at least "in principle."

This kind of treatment of matters dear to the hearts of kineticists has led Fristrom and Westenberg to apply the adjective "execrable" to the "global" kinetics so dear to the hearts of combustion and pyrolysis men. But the latter aren't the only ones who are guilty of this chicanery. If this be sin, we can derive consolation from the knowledge that we sinners are probably in the majority.

On the other hand, one might, with some justification argue that the formalism of chemical kinetics is unrealistic and that even the simplest of the chemical reactions in which there is intrinsic interest are too complicated for the formalism of classical kinetics. The kinetics related sciences make use of many kinds of ideas applied to solve a vast conglomeration of problems ranging from intra-atomic energy transitions to reaction schemes of literally global magnitude. What is basic depends on where one chooses to enter the conglomeration. We may be trying to push a camel through a needle's eye if we insist that we describe the processes that take place in flames and in pyrolizing solids using the same concepts that can be applied to the homogeneous, gradient free systems in which kinetic parameters are usually defined. Ultimately, there should be some kind of convergence—a sort of correspondence principle—but I think that combustion and pyrolysis are often the losers if we insist on a blind allegiance to the formalism of kinetics as a necessary prerequisite to a claim that we understand combustion. If the kineticist gets too hard to get along with, we can always point out that his assumptions about the state of his molecules look worse and worse as we take a closer and closer look at them. An ox has fleas to plague him, and the flea has other fleas to plague him ad infinitum.

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[2] For example: (B. E. Dahnecke, S. J. Wiersma, and E. A. Fletcher, unpublished work). The rate of formation of ClF from $Cl_2 + F_2$ is well represented by the equation:

$$\frac{d[\text{ClF}]}{dt} = \frac{2k_A[\text{F}_2][\text{Cl}_2]^{1/2}}{\left\{1 + \frac{k_B[\text{Cl}_2]}{[\text{F}_2]} + \frac{k_C[\text{ClF}]}{[\text{F}_2]}\right\}^{1/2}}$$

where

$$k_A = (k_1 k_2 k_3 / k_4)^{1/2}$$

$$k_B = k_2 k_6 / k_3 k_4$$

$$k_C = k_7 / k_3$$

The numbered k's are specific rate constants for the elementary reactions that go to make up the mechanism of the overall reaction. "Activation energies" associated with the lettered k's can be computed from the activation energies of the numbered k's, but the numbered k's are the only ones whose activation energies have mechanistic significance. An "activation energy" of the overall reaction can be formally computed, but its magnitude depends on the initial mixture composition and the extent of the reaction. Nevertheless, it may be a very useful thing to know, if one wants to know something about the behavior of chlorine-fluorine mixtures—spontaneous ignition limits, for example.

We adopt, then the point of view that the study of the kinetics of combustion processes is a useful, worthy discipline in its own right. It is best studied in combustion systems. The kinetics of other kinds of complex processes are best studied in the systems to which these processes apply. Whenever we can, we try to relate the kinetics to the formalism of classical chemical kinetics. In complicated systems, it is questionable whether information about the rates and mechanisms of the so-called elementary reactions is more important or useful than other kinds of information in helping us understand many kinds of phenomena such as ignition, flame propagation, or quenching, although as was pointed out before, such information has been used in a few cases to rationalize experimental observations.

The formal definitions of transport coefficients and rate constants don't really apply to the systems we deal with. How can you talk about the variation of thermal conductivity or a rate constant—in a reacting system with concentration gradients in it, when the concept of temperature, especially as it applies to conductivity or reaction kinetics is not clearly defined for such a system—without compromising your principles? You can't. All sorts of dodges, many of them useful, have been employed to permit us to retain our formalisms, but they don't change the fact that many of the formalisms we are used to using become intractible—indeed, are not realistic—when we try to apply them to real systems.

Keeping that sort of thing in mind, my students and I set out several years ago to study some combustion phenomena in what we hoped would be simple systems. Fluorine (occasionally ClF_3) was our oxidant. The studies are still in progress and it's sometimes foolish to write about things while you're still thinking about them. We know we've sinned. Please forgive us.

2. Combustion Phenomena Studies

The studies fall conveniently into three categories:

(1) Fluorocarbon combustion studies in which variations of the molecular structure of the fuel are found to be very important in determining flame speeds and flammability and detonation limits, and in which the kinetics seems to depend on the ease of an initial attack on the fuel molecule. Larry Ambs, Jerry Hinderman and David Kittelson did most of the work here.

(2) Freon combustion studies, in which it appears that:

(a) Flame speeds of CF_3Cl–F_2 mixtures seem to be much more sensitive to the preexponential terms than they are to the exponential term which is the darling of the thermal theories.

(b) Flame speeds and quenching behavior of $BrCF_3$–F_2 mixtures are much more dependent on transport phenomena than they are on chemical kinetics. Donald Parks did this work.

(3) Chlorine combustion studies in which it appears that even when such phenomena as spontaneous

ignition limits and flame speeds can be well correlated with the formalisms of chemical kinetics the pre-exponential terms and activation energies are not necessarily the same, nor do they necessarily have the same significance. Larry Ambs, Barton Dahneke and Steve Wiersma contributed to this part.

2.1. Fluorocarbon Combustion Studies

Fluorocarbons burn nicely in chlorine trifluoride [11] or fluorine [12, 13, 15] and some will burn nicely in oxygen as well [13, 14]. The oxygen flames are probably more complicated than those supported by fluorine but even these are much simpler than hydrocarbon flames [16]. When hydrocarbons burn in air, their combustion behavior, flame speeds, ignition limits and quenching distances, for example, are all pretty much the same [17] suggesting that the nature of the individual fuel is of little importance. Differences which might be caused by variations in the kinetics are washed out by other factors. Even finely divided non-volatile liquid hydrocarbon aerosols have about the same flame speeds as those of the gaseous hydrocarbons. There are so many reactions possible and going on at once that the important kinetics in hydrocarbon oxidation reactions apparently takes place in that part of the flame that consists of the partially oxidized fragments of the fuel molecules in a melange that is pretty much the same regardless of where the components came from originally. In contrast, flame speeds, ignition limits and energies, and quenching distances are quite different in different fluorocarbons [11].

Maximum flame speeds in hydrocarbon-air mixtures occur in compositions near those which give maximum flame temperatures [17]. In fluorocarbon-oxygen [14, 19] and freon-fluorine flames [20], maximum flame speeds seem to be favored by equimolar concentrations of reactants even though this composition may be quite far from that which gives the maximum flame temperature. This observation suggests again that there is something quite different in the way kinetics enters into fluorocarbon combustion in comparison with hydrocarbon combustion.

Perfluoroethane-ClF$_3$ can be ignited only with some difficulty and burns only between relatively narrow composition limits. The flame speed is low—of the order of 10 cm/s. Perfluoropropane-ClF$_3$, burns over a range of compositions comparable to that of hydrocarbons and at hydrocarbon-air flame speeds. Perfluorocyclobutane-ClF$_3$ and cyclo-C$_4$F$_8$-F$_2$ mixtures are very easy to ignite over a wide range of compositions. They detonate over practically the entire combustible range. The problem is frequently to keep them from igniting prematurely. The flame temperatures of the three fuels are in the same order as their reactivities so one is tempted to attribute their combustion behavior only to the effect of flame temperature on the "global" rate. Many hydrocarbon-based fuels behave as if the details of the reaction mechanisms are unimportant—the flame

speeds depends only on the temperatures [21] and global kinetics works well.

Nevertheless, Jerry Hinderman sought to get some idea of the relative "global" reaction rates of these fuels burning in fluorine. His technique was to burn equimolar mixtures of the fluorocarbons with varying amounts of fluorine present in amounts insufficient to burn the fuels to completion and to examine the combustion products gas chromatographically. The results were surprising. We weren't able to deduce relative rates. The differences were so great that one of a pair of fuels was usually completely used up before the other had started reacting. An example of the kind of results that we observed is shown in figure 1.
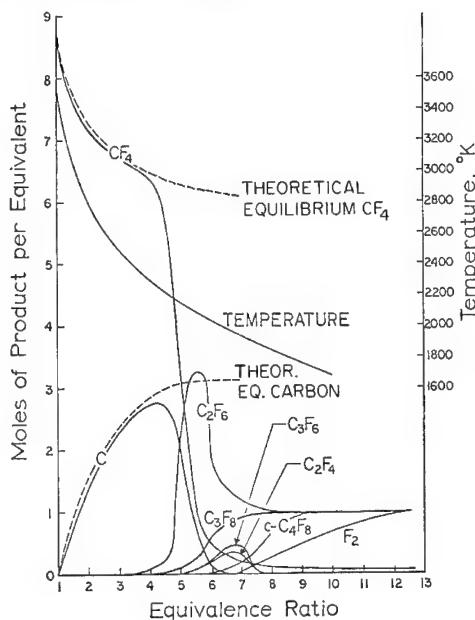
FIGURE 1. *Product-composition from a mixture containing equimolar amounts of C$_2$F$_6$, C$_3$F$_8$ and cyclo C$_4$F$_8$*

Figure 1 presents the product composition which resulted from the explosion of equimolar mixtures of C$_2$F$_6$, C$_3$F$_8$ and cyclo-C$_4$F$_8$ with various amounts of fluorine. The ordinate shows the number of moles of each of the products which was produced from an amount of mixture which contained one mole of each of the reactants, i.e., 9 gram-atoms of carbon. The amount of fluorine is shown on the abscissa, which gives the equivalence ratio. For example, an equivalence ratio of 2 means that there was half as much fluorine present as would have been necessary to burn the fuels completely to CF$_4$ in an isothermal reaction. (In the adiabatic reaction, dissociation products are, of course, present.) The figure also shows the calculated adiabatic constant volume equilibrium flame temperature's variation with composition and the low temperature equilibrium composition of the products. The results are interesting for several reasons.
(1) They clearly illustrate that the differences in the combustion behavior are associated with vast

differences in the rates at which there is an initial disruption of the molecule under the conditions of flame propagation. As the fluorine concentration (and flame temperature) is reduced, C_2F_6 stops reacting first although a 2200 K flame which consumes all of the C_3F_8 passes through it. Then C_3F_8 stops reacting when the flame temperature is much lower (because adiabatic equilibrium conditions are not achieved) although almost all of the C_4F_8 is consumed, and finally, unreacted C_4F_8 begins to appear among the products when the temperature is quite low. Clearly, because of the limited number of things a fluorocarbon molecule can do in reacting with fluorine the course of the action depends on first breaking a carbon-carbon bond. Once that has happened, what follows happens quickly.

(2) The results also suggest that at lower temperatures (and perhaps early in the reaction) the principle reaction is C–C scission followed by recombination of the scission fragments and/or reaction with available fluorine. There seems to be very little evidence for breaking of C–F bonds which would result in disproportunation and formation of CF_4 and carbon. Thus, C_3F_8 decomposes to yield, ultimately one mole of C_2F_6 and cyclo-C_4F_8 yields another. At the lower temperatures, C_4F_8 yields primarily the scission products, C_3F_6 and C_2F_4, just before, with further reduction in fluorine content the mixtures stop burning or support only very weak flames. At an intermediate composition C_3F_6 and C_2F_4 are produced in just the right proportions to suggest that the cyclo C_4F_8 ring breaks to produce C_3F_6 and a CH_2 radical.

(3) With the higher fluorine concentrations (and temperatures) the C–F scission reactions which lead to disproportionation and chemical equilibration become important as is evidenced by the formation almost exclusively of CF_4 and carbon.

I'm not sure what a global reaction rate means with this particular family of compounds. The combustion behavior clearly must depend primarily on the initial pyrolysis of the fuel molecule. There is no way to relate a "global" reaction rate or an instantaneous reaction rate to temperature because the concept of an "extent to which the reaction has gone to completion" is meaningless insofar as an application to the kinetics of the reaction is concerned, and the rates of the reactions which follow the initial C–C bond rupture are probably fast enough that they are relatively unimportant in determining combustion behavior. When the oxidant is oxygen, however, the other reactions probably become important as is suggested by the fact that the maximum fundamental flame speed in cyclo C_4F_8–O_2 mixtures occurs not where the flame temperature is highest, but where the equilibrium F concentration is a maximum [14].

2.2. Freon Combustion

The fluorine supported combustion of CF_3Cl demonstrates how differently the kinetics and transport coefficients interact in deflagration through hydrocarbon-air and through CF_3Cl–F_2 mixtures; the fluorine supported combustion of argon and helium diluted CF_3Br might be cited to "prove" that these propagation processes' behavior is almost completely dominated by the transport coefficients.

Some of the characteristics of CF_3Cl–F_2 flames are shown in figure 2.
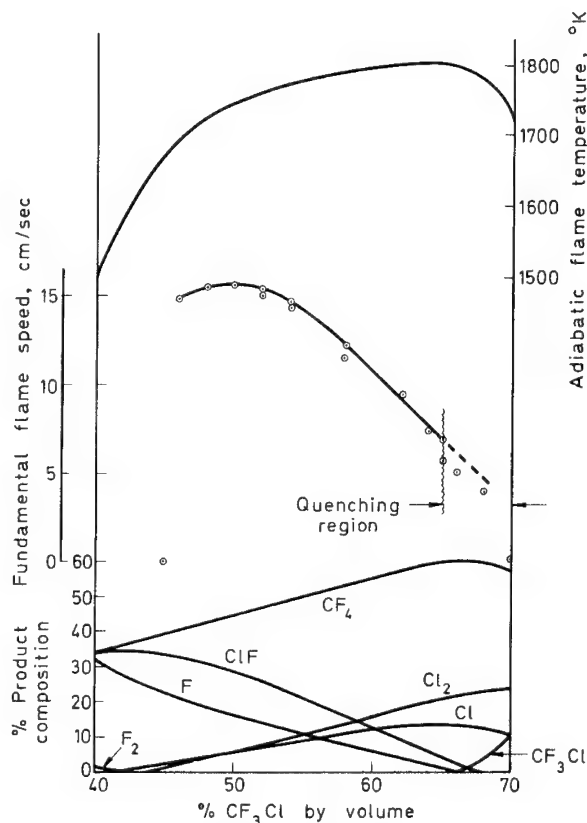
FIGURE 2. *Burning velocities, equilibrium temperatures, and product compositions of CF_3Cl-F_2 flames.*

The flame temperature maximum occurs near the rich limit, and the maximum flame speed at a composition corresponding to equimolar amounts of the reactants. Evidently the augmentation of the reaction rate constants associated with the higher flame temperature is not great enough to compensate for the adverse effect on the stoichiometry in the colder part of the flame or possibly the higher concentration of the low-molecular-weight F in the leaner mixtures. In hydrocarbon-air, highest flame speeds are associated with highest temperatures.

If one were to examine the results for the very dilute flames of CF_3Br–F_2 mixtures separately, one might be tempted to say that global kinetics works nicely in describing the effect of the diluent on the behavior of CF_3Br–F_2–Ar and CF_3Br–F_2–He mixtures. But the variation we have chosen to describe is completely dominated by transport properties, as is evident from an examination of all the data. A knowledge of the kinetics is unimportant for an-
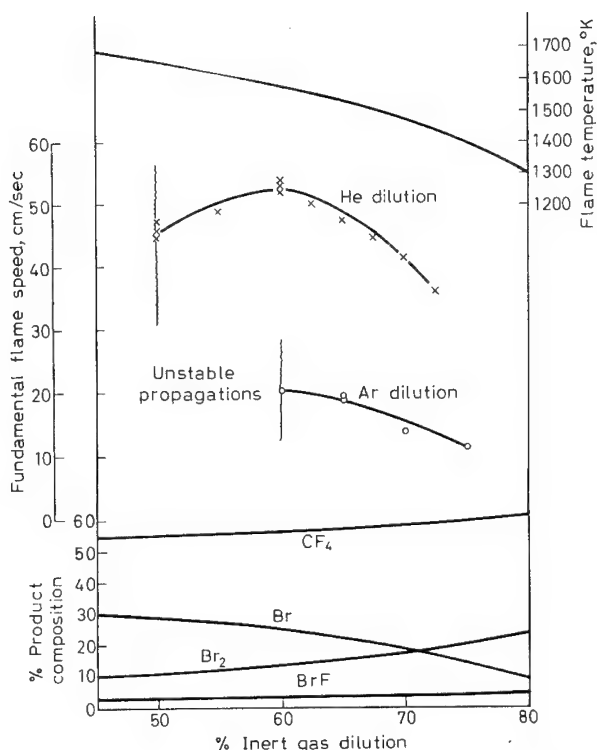
FIGURE 3. *Burning velocities, equilibrium temperatures and non-inert product compositions of 65 per cent CF₃Br-F₂ flames diluted with argon (lower curve, circles) and helium (upper curve, x's).*

swering only the question we've asked. Figure 3 shows the behavior and properties of such flames. Mixtures which differ from each other only in the nature of the monatomic-inert diluent have the same flame temperatures, product composition, and, very likely, "reaction-rates". Yet, as can be seen in figure 3, the fundamental flame speeds are quite different. Dilution by the low-molecular-weight helium at first increases the flame speed because it increases the rate of heat transfer from the products to reactants. Further dilution decreases flame speed because it reduces both temperature and reactant concentrations. Argon-diluted mixtures have much lower flame speeds. Deflagration theories, such as the Zeldovitch-Frank-Kemenetsky-Semenov theory, which use average (global) reaction rates predict that, if the global rates are the same, flame speeds should be proportional to thermal conductivities, and if one compares the very dilute argon and helium mixtures described here, the "confirmation" of the theory is quite striking. One might even be tempted to use such a flame for measuring the rate of the reaction.

2.3. Chlorine-Fluorine Studies

The simplest fluorine supported combustion system we have worked with is the Cl_2–F_2 system. We have studied low temperature kinetics, spontaneous ignition limits, flame structure and some

fundamental flame speeds. The kinetics of the reaction is well described by seven elementary reactions:

I. $F_2 + M \xrightarrow{k_1} 2F + M$ $\Delta H = 38$ kcal

II. $F + Cl_2 \xrightarrow{k_2} ClF + Cl$ -3

III. $Cl + F_2 \xrightarrow{k_3} ClF + F$ -23

IV. $Cl + F + M \xrightarrow{k_4} ClF + M$ -61

V. $F + F + M \xrightarrow{k_5} F_2 + M$ -38

VI. $Cl + Cl + M \xrightarrow{k_6} Cl_2 + M$ -58

VII. $Cl + ClF \xrightarrow{k_7} Cl_2 + F$ $+3$
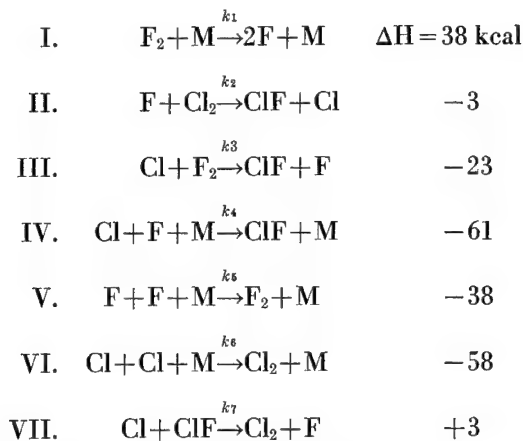
The rate of either the isothermal reaction or that used in the interpretation of the spontaneous explosion limits is well represented by

$$\frac{d[ClF]}{dt} = \frac{2\left(\frac{k_1 k_2 k_3}{k_4}\right)^{1/2} [F_2][Cl_2]^{1/2}}{\left(1 + \frac{k_2 k_6 [Cl_2]}{k_3 k_4 [F_2]} + \frac{k_7 [ClF]}{k_3 [F_2]}\right)^{1/2}}$$

In applying the rate expression to the explosion limits, one makes use of the fact that the system is committed or not committed to an explosion before the reaction has gone to the extent of 1 percent. The third term in the denomenator is therefore unimportant and if one has started with a stoichiometric mixture, for example, the "rate constant" of the reaction is

$$k = \frac{2\left(\frac{k_1 k_2 k_3}{k_4}\right)^{1/2}}{\left(1 + \frac{k_2 k_6}{k_3 k_4}\right)^{1/2}}$$

and the activation-energy which can be computed from tabulated [22] values of the activation energies or reasonable estimates of k_1–k_7 turns out to be about one-half of the activation energy of reaction I, which is in good agreement with the value deduced from the application of Semenov thermal explosion theory to the experimental observations, 18.65 kcal. The magnitude of the activation energy thus has an appealing mechanistic significance—it is a nice activation energy. When we consider the isothermal reaction and wish to describe the kinetic behavior over a wide range of compositions, the reaction stops being nice. The "activation-energy" may be said to depend on the extent of reaction as well as on the initial composition of the mixture if we try to find a simple formula that will give us a temperature dependence of the reaction rate. If we assume that

the third term in the denomenator is large, we get the rate expression

$$\frac{d[\text{ClF}]}{dt} = k' \frac{[\text{F}_2]^{3/2}[\text{Cl}_2]^{1/2}}{[\text{ClF}]}$$

which correlates the experimental observations with a correlation-coefficient of about 0.99 for the appropriate values of k'. But if we make a conventional $\ln k$ versus $1/T$ plot to determine the activation energy of this reaction, it is about 25 kcal. The difference here results not from a change in mechanism but because in one case our "global kinetics" describes what is important in the process we are dealing with, and, in the other, what is important just happens to be well represented by a formula that has the same form as a simple kinetic equation. It's ironic here that the more appealing result comes from an abominable combustion process and the less appealing result comes from the clean, isothermal experiment.

It's customary in presenting a paper like this to draw conclusions. I'm reluctant to do it because the study of the kinetics of combustion-processes is an extremely lively one now, and you imply that an end has been reached when you draw a conclusion. In kinetics, as in combustion, one frequently gets the idea that we attack fundamental problems simply because they are there. We usually rationalize our efforts by saying that we can describe anything when we really understand the fundamentals. I'd say the state of the art of combustion is not that well advanced. I think its most useful to make use of whatever information you can get. Most frequently the kind of information you will need will depend on where you want to go from where you are. If you can describe your system well enough so that you can use the "exact" physical quantities that are defined in terms of the formalisms we like to use, that's fine. If you can't, but you have a good formula that gives useful answers using execreble kinetics—so be

it. We can probably find a set of coordinates somewhere that makes it basic if we look for it.

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Burning of Polymers

C. P. Fenimore and F. J. Martin

General Electric Corporate Research and Development, Schenectady, New York

After a rod of solid polymer mounted vertically in a slowly rising stream of oxidant/inert gas mixture is ignited at the top end, the oxidant content of the mixture may be varied until that composition is found which will just support burning down the whole length of the sample. For many polymers this limiting volume-fraction of oxidant can be determined with a precision of about one percent and it serves as a convenient measure of flammability of the material.

Experiments show that the simplest model for such burning is one in which the oxidant does not react directly with the polymer, but is consumed in a nearby flame zone which heats and pyrolyzes the polymer to yield fuel gases. This model appears to be valid for some systems, but not for others.

Experiments may be carried out in which the compositions of the sample and the oxidizing atmosphere are varied in a systematic way. The measured flammabilities, together with a simple model of the burning process permit inferences about the manner in which composition variations affect the burning. The mode of inhibition by flame retardant additives may be inferred in this way.

For example an inhibitor which interferes directly with the gasification of the condensed phase should work independently of the flame reactions for the simple two-stage candle-like burning; it should still inhibit when the polymer is burned in N_2O rather than O_2. Such has been observed when chlorine has been substituted into polyethylene.

By contrast an inhibitor which poisons the flame reactions may be specific for reactions with oxygen and not work with another oxidant such as N_2O. Such is the case for Sb_2O_3 added to slightly chlorinated polyethylene.

Effects of different inert gases, of initial temperature and of pressure have also been observed.

Key words: Burning of polymers; flame retardants; flammability.

1. Introduction

The burning of organic solids in air is a complex phenomenon involving high-temperature gas phase reactions, convection and conduction of heat, diffusion of gaseous species, and chemical reactions in the condensed phase at and in the vicinity of the burning surface. In general, burning is not a steady-state phenomenon. Some or all of the component processes will depend strongly upon sample geometry, size and dimensions of surrounding enclosure (if any), physical and chemical properties of the sample, nature of ignition and elapsed time from ignition.

From the technological point of view, it is important to be able to determine and to predict the effects of these various parameters on the burning process—and particularly on the rate of burning and the nature of the products.

It is the purpose of this paper to discuss the information that can be derived from simple experiments with candle-like flames together with a very simple model for such flames.

2. Model for Candle-like Flames

If one holds a rod of high-molecular-weight polyethylene (PE) or cast polymethylmethacrylate (PMMA) vertically in a suitable gaseous oxidizing atmosphere and ignites the top end, it is found that the rod burns much like a candle [1, 2].[1] Such a flame for polyethylene burning in oxygen-deficient air is shown in figure 1. A clear molten dome at the top of the rod is surrounded by a thin blue flame with a yellow cap arising from thermal emission from soot particles. A few drops of molten polymer have run down the side of the stick and frozen.

Burning experiments of this kind are conveniently carried out in a vertical Pyrex chimney about 7.5 cm I.D. by 45 cm high, although the dimensions are not critical. The specimen is mounted vertically on the chimney axis roughly midway up. The oxidizing atmosphere is prepared outside the chimney by metering and mixing the components in a flowing system; it then enters the chimney from the bottom through a bed of glass beads which serves to smooth the flow. The upward gas flow is kept steady in the range 3–12 cm/s, which serves to sweep smoke and products out of the chimney. Test equipment of this sort is now commercially available.

The size of the flame varies with the oxygen content of the air and becomes very large in pure oxygen. As the oxygen content of the air is decreased, the flame size decreases until a concentration is

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[1] Figures in brackets indicate the literature references at the end of this paper.
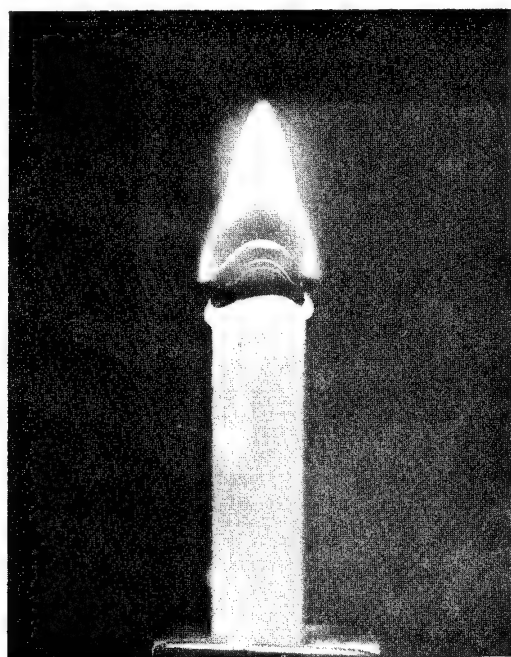
FIGURE 1. *Polyethylene burning close to extinction limit at 1 atm.*

Oxygen index = 0.175. Upward gas velocity 8 cm/sec. Stick about 8 mm wide.

1. BURNING SPECIMAN
2. CLAMP WITH ROD SUPPORT
3. IGNITER
4. WIRE SCREEN
5. RING STAND
6. GLASS BEADS IN A BED
7. BRASS BASE
8. TEE
9. CUT-OFF VALVE
10. ORIFICE IN HOLDER
11. PRESSURE GUAGE
12. PRECISION PRESSURE REGULATOR
13. FILTER
14. NEEDLE VALVE
15. ROTAMETER

GLASS COLUMN (MINIMUM DIMENSION 45CM H. × 7.5CM I.D.)

METAL SHROUD
(OPENING DIAM. = 5CM)

GLASS COLUMN

SECTION A-A

OPTIONAL DEVICE FOR RESTRICTING COLUMN OPENING

OXYGEN
NITROGEN

ALTERNATE FLOW MEASURING DEVICE

FIGURE 2. *Typical apparatus for oxygen index determinations.*

TABLE 1. *Selected oxygen indices*

	n
Hydrogen (4)	0.054
Ethylene (4)	0.105
n-Paraffins (C_3 to C_{10}) (4)	0.127 to 0.135
Benzene (4)	0.133
Polyoxymethylene Delrin or Celcon	0.157
Kitchen Candle	0.16
Polymethylmethacrylate Rohm and Haas Plexiglas	0.174
Polypropylene Hercules Profax 6505	0.174

Asbestos-filled "slow-burining"
   Polypropylene
   Union Carbide JMDC-4400
	0.205

"Self-extinguishing" Polypropylene Union Carbide JMDA-9490	0.282

Polyethylene
   Allied Chem 1220 or Phillips Marlex 5002
   Marlex filled with 50 wt % Al_2O_3
   Marlex filled with 60 wt % $Al_2O_3 \cdot 3H_2O$
	0.174
	0.196
	0.302

Polystyrene	0.181

Epoxy* unfilled
   Filled with 50% Al_2O_3
     Norton 38900
   Filled with 60% $Al_2O_3 \cdot 3H_2O$
     Alcoa C-333
	0.198
	0.250
	
	0.408

Polyvinyl Alcohol DuPont Elvanol 70-05	0.225
Polyvinyl Fluoride DuPont Tedlar	0.226
Chlorinated Polyether Hercules Penton [—$CH_2C(CH_2Cl)_2CH_2O$—]	0.232
Polycarbonate General Electric various clear Lexans	0.26–0.28
Polyphenylene Oxide General Electric [—$C_6H_2(CH_3)_2O$—]	0.28–0.29
Silicone Rubber Silica-filled General Electric SE9029	0.30
Polyvinylidene Fluoride Kynar	0.437
Polyvinyl Chloride Geon-101	0.47
Polyvinylidene Chloride Dow, Saran	0.60
Polytetrafluoroethylene DuPont, Teflon	0.95

Loosely Woven Fabrics
   Cotton
   Wool
	
	0.185 ± .005
	0.238

Synthetic 60/40 = vinyl chloride/
   acrylonitrile
   Dynel
	0.298

* Epoxy was 100 parts Epon-826, 75 parts hexahydrophthalic anhydride, 1 part DMP30, cured 16 hours at 400 K

reached such that the flame after ignition will no longer propagate down the whole length of the stick. Experimentally one can determine a limiting oxygen concentration such that a small flame propagates down the whole length of the stick in a nearly steady-state manner; any reduction in oxygen would result in extinction. This limiting concentration expressed as the volume fraction of oxygen in the atmosphere is called the oxygen index of the material burned. It has proven to be a convenient rating of polymer flammability, and a standard ASTM test procedure D2863-70 has been set up for determining it [3]. Some oxygen index values are given in table 1. An apparatus sketch taken from the ASTM test instructions is shown in figure 2.

The lower the index, the more flammable the material. There are some experimental limitations which will be discussed later, but the index is often reproducible to about one percent, and for many (but not all) materials largely independent of specimen dimensions and upward gas velocity over considerable ranges of these variables. (The same index was previously defined and used by Wolfhard and coworkers [4, 5] as a measure of flammability of volatile fuels and gases burning as diffusion flames.)

The flame for a rod of cast polymethylmethacrylate (PMMA) at the lower oxygen limit looks much like that for PE except that there is less melting and dripping and more bubbling at the burning surface. The flame for PMMA propagates down the rod with very little change in appearance or velocity with time; and hence closely approaches a true steady state.

When a rod of cured epoxy resin heavily filled with hydrated alumina is burned at the lower oxygen limit, a zone of glowing alumina works its way steadily down through the specimen with little visible flame; this perhaps represents an example of a surface combustion process [6].

Such observations suggest a simple, steady-state model for candle-like flames burning close to the extinction limit. The gaseous oxidant is supposed not to react directly with the polymer but is consumed in a nearby combustion region which heats and pyrolyzes the polymer, and thus generates the fuel for the combustion region. The combustion region may be a diffusion flame surrounding the polymer as discussed above for PMMA; or it might be a region of surface combustion, as with a polymer filled with a nonburning inorganic material.

Gas analyses and temperature measurements through the flame above rods of PMMA, and POM (burning at reduced pressure to spread out the flame) support the model [7]. The materials are known to pyrolyze largely to the monomer. Some of the data are summarized in table 2; experimentally determined temperatures and gas concentrations above burning PMMA are shown in figure 3. Within the approximations involved, the estimated heat transfer by conduction and radiation from the flame to the polymer surface is sufficient to warm the surface of the polymer to the observed temperature and to depolymerize the material to form fuel gases at the observed rate; in this way steady-state candle-like burning is sustained. In the case of PE the primary pyrolysis products are unknown so that it cannot be certain that the model applies, but it seems likely.

On the other hand, as seen in table 2, when warm PTFE rods are burned in concentrated O_2/Ar mixtures at 1 atm, the heat conducted and radiated

TABLE 2. *Heat fllow from flame to the condensed phase for polymers burning in Ar-O_2 atmospheres**

Polymer (cross section) of rod	Surface temperature	Fraction of Carbon as Monomer, 0.1 cm above tip	Burning Rate cm/sec × 10³	Heat Conducted to Polymer kcal per monomer unit		Observed Heat Conducted as Fraction of Total Heat of Combustion
	K			Obs.	Calc**	
Methylmethacrylate 0.36 cm²	850	70	2.6	30	38	0.05
Formaldehyde 0.36 cm²	750	33	2.3	15	17	0.14
Tetrafluoroethylene						
11.3 cm²	. . . .	21	5	. . . .	50	. . . .
4.9 cm²	920	13	7	. . . .	50	. . . .
2.8 cm²	920	5	7	13	50	0.12
1.2 cm²	920	0	8	. . . .	50	. . . .
Ethylene 0.36 cm²	900	30	1.8	20	. . . .	0.07

* Burned at 0.07 atmos P in 20–22 percent O_2 except for polytetrafluoroethylene which was burned at 1 atmos in 88–100 percent O_2 after being preheated to 400 K.

** Heat of gasification to monomer (21.4 kcal for methylmethacrylate (12), 13 for formaldehyde (13), 41.1 for tetrafluoroethylene (14) plus estimated heat to warm to surface T gives this column.

from the flame back to the condensed phase falls far short of that required to further warm and depolymerize the polymer at the rate necessary to sustain the observed steady-state burning. In this case heterogeneous reactions with species in the gas phase must contribute to the polymer gasification. The gaseous species may be O_2 or O or more likely in some cases it is flame-generated F atoms which are calculated to be a major flame species at equilibrium. Thus, the simple candle-like burning model in which only heat is transferred by conduction and radiation from the flame to the burning surface is not valid for PTFE [8].

3. Effects of Different Inert Gases in the Atmosphere

If one burns in a candle-like manner similar samples of a given polymer in atmospheres that differ in the inert gas present, it is found that the mole ratios oxygen/inert gas at the lower oxygen limit vary linearly with the heat capacities of the inert gases when the latter are Ar, N_2 or CO_2 [9]. Data are
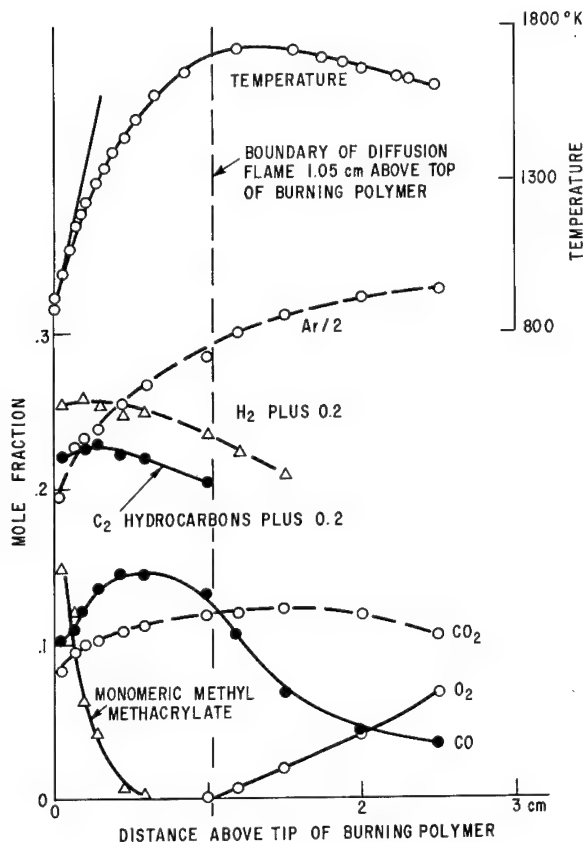
FIGURE 3. *Gas composition and temperature along the central axis above a polymethyl methacrylate rod, 0.36 cm² cross section, burning at 5 cm of mercury pressure in argon-oxygen, 20 percent O_2.*

Distances are measured from the burning tip, and the dashed line at 1.05 cm shows the position of the visible diffusion flame. The limiting temperature gradient at the surface is 2500 K cm⁻¹. For clarity, H_2 and C_2 hydrocarbons are displaced 0.2 upwards.
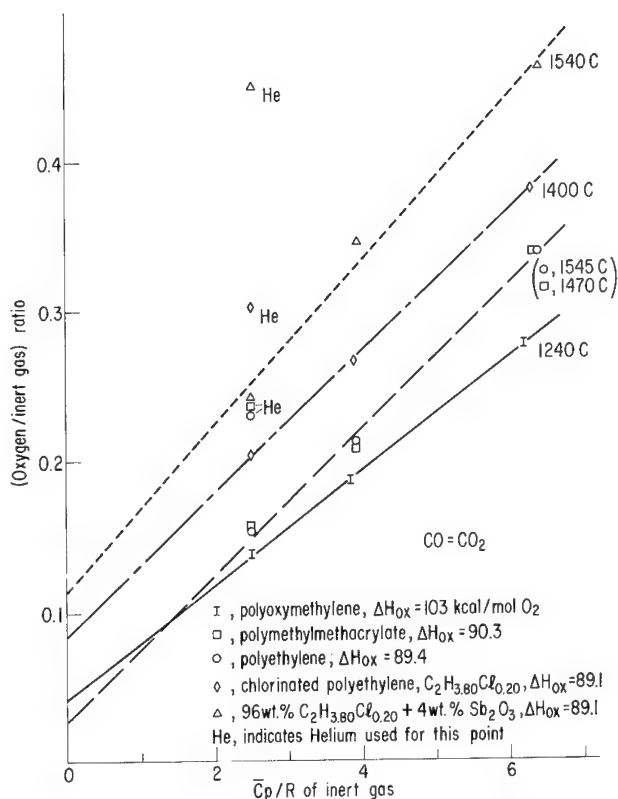
FIGURE 4. *Effect of heat capacity of inert gas on (oxygen/inert gas) ratio.*

ΔH_{ox} is estimated heat of combustion per mole of O_2 for reactions written to produce equimolar quantities of CO and CO_2. Calculated flame temperature to right of curves.

shown in figure 4. It is noteworthy that curves have an intercept on the n_{ox}/n_i axis.

We propose the following model to explain these data:

a. For stability the flame must attain a minimum temperature which is independent of the inert gas in the atmosphere.
b. The stoichiometry of the overall flame reactions (and hence the heat release per mole of oxygen consumed) is independent of the inert gas.
c. The flame is nonadiabatic. The mean rate of heat loss per mole of mixed hot products and inert gas is independent of the inert gas. By heat loss we mean heat transferred outside the flame by radiation or conduction to the atmosphere. It does not contribute to heating the preflame gases.

For this model a simple heat balance may be written as follows:

$$[n_{pr}C_{p,pr}+n_iC_{p,i}](T_2-T_1)=n_{ox}\Delta H_{ox}-(n_{pr}+n_i)Q$$

$$(1)$$

where:

n_{pr} = flux of products from flame zone, moles/s.
n_i = flux of inert gas through flame zone, moles/s.

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n_{ox} = flux of oxygen into flame zone, moles/sec.

C_p = heat capacity per mole.

T_2 = flame temperature.

T_1 = initial temperature of sample and atmosphere.

ΔH_{ox} = enthalpy decrease for reaction of one mole of O_2 at T_1.

Q = mean heat loss per mole from flame zone gases. It is taken to be constant for flames of a given material and burning at the same initial conditions.

Equation (1) may be rearranged to give:

$$\frac{n_{ox}}{n_i} = \frac{Q}{B} + \frac{T_2-T_1}{B} C_{p,i} \qquad (2)$$

where $B = \Delta H_{ox} - \dfrac{n_{pr}}{n_{ox}} \left[-Q + C_{p,pr}(T_2 - T_1) \right]$ and

represents the net heat available to warm the inert gas per mole of O_2 consumed. (Here heat loss per mole from product gases alone is taken to be equal to that from the whole hot mixture; it is an approximation.) The quantity Q/B represents the fraction of heat available to the inert gas which is lost from the flame.

To the three points determined for Ar, N_2 and CO_2 one may fit a straight line; this in turn gives values for Q/B and $(T_2-T_1)/B$. For an assumed value of the heat release, ΔH_{ox}, one can then solve for Q and for T_2-T_1. The temperature values in figure 4 were obtained in this way. Clearly if the flame were adiabatic, Q would be zero and a curve of n_{ox}/n_i versus $C_{p,i}$ would pass through the origin. This is not observed.

The derived temperatures and heat losses appear reasonable and lend support to the assumptions made in the model. Estimates of the fraction of the heat of combustion lost run generally between 10 and 40 percent.

Thermal conductivity values for Ar, N_2, and CO_2 (which are generally the major components of the product mixture) vary by a factor of two or less. On the other hand, the thermal conductivity of He is higher by a factor of eight or so. The n_{ox}/n_i values measured in helium/oxygen for PE, PMMA and chlorinated PE are 1.50 times those measured in Ar/O_2 even though He and Ar have identical molar heat capacities. For chlorinated PE plus 4 wt percent Sb_2O_3 the corresponding ratio is 1.86. It seems reasonable to attribute the higher values in helium to greater heat losses from the flame. The higher sensitivity of chlorinated PE plus Sb_2O_3 to He may be attributed to slower gas phase reactions for this material and hence relatively greater heat losses. Other work supports the idea that Sb_2O_3 inhibits by slowing down gas phase reactions.

Finally, from a practical point of view, we may rate the various inert gases for effectiveness in quenching flames in the order of ascending n_{ox}/n_i values; the higher n_{ox}/n_i, the more effective the gas as a flame quencher. On this basis, $CO_2 > He > N_2 > Ar$ for the flames studied. This is the same order of
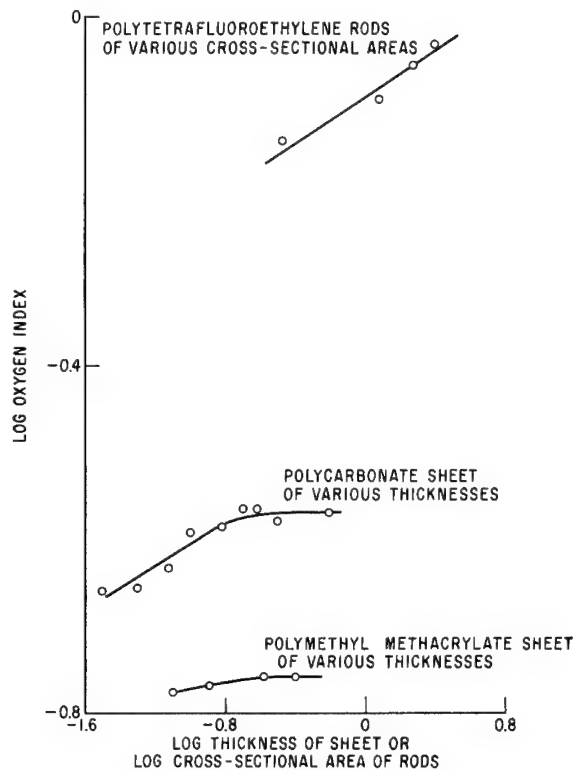
FIGURE 5. *Effect of size of burning specimen.*

Polycarbonate data from Ref. 15.

effectiveness as that reported for increasing the quenching distance in helium-oxygen-inert gas mixtures [10].

4. Effect of Some Variables on the Oxygen Index

The indices of polymers are nearly independent of the oxidant gas velocity in the range 3 to 12 cm/s—possibly because flame-generated convection currents in the neighborhood of the test specimen always exceed these values anyway. However, there is a small dependence on gas velocity and for comparison purposes a gas velocity of 4 cm/s has been set for the ASTM-D-2863-70 test procedure.

For PE, PMMA, polystyrene (PS) and possibly for most other unfilled thermoplastics, the indices are independent of sample thickness in the range 0.2 to 1.0 cm and decrease only slightly for smaller thicknesses. However, for polycarbonate (PC) sheet less than 0.2 cm thick, the index falls rapidly with decreasing thickness; it varies as thickness to about the 0.13 power. Data are shown in figure 5. Polytetrafluoroethylene (PTFE) rods show a similar dependence of index on cross-section area even for large specimens [8]. It is possible that the greater dependence of index on sample size is associated with a mode of burning involving heterogeneous reactions in the flame zone.

Despite the size effect, reproducible values of the index can be obtained for most thin films and fabrics
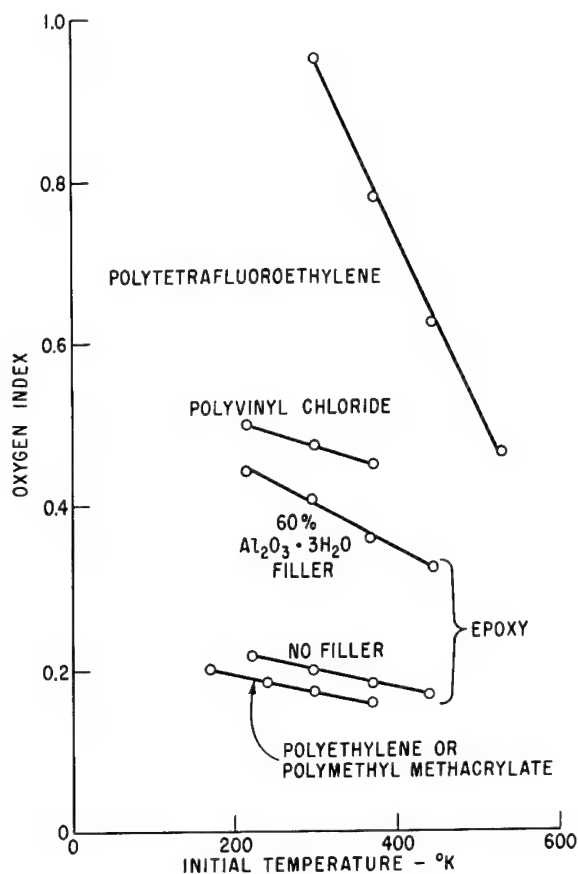
FIGURE 6. *Effect of initial temperature.*

which do not melt too badly ahead of the flame [11]. This is conveniently done on a strip of material about 15 by 5 cm (dimensions not critical) clamped along the vertical long edges in a light metal U-frame. The sample is ignited uniformly along the top open end of the U; and the index is determined in the same manner as for solid rods. The metal frame serves to support the sample and to suppress rapid burning down along the otherwise free edges. Some results are included in table 1.

By jacketing the apparatus and precooling or preheating the gas and polymer sample, the effect of initial temperature on the index can be studied. Data are shown in figure 6.

By modifying the apparatus to permit burning under a controlled pressure, the dependence of index on pressure can be determined. In figure 7, the index for polytetrafluoroethylene is seen to vary nearly inversely as the $\frac{1}{2}$ power of the pressure. For POM, PE, and PMMA the dependence is much smaller.

One might wish to evaluate an index for upward burning of a sample after ignition at the bottom end. Such an arrangement would maximize convective heat transfer to the unburned material, in contrast to the usual downward burning where convective heat transfer is at a minimum. However, only a few materials will withstand the drastic preheating associated with upward burning long enough to

permit meaningful measurements; more often the samples drip and sag too badly. For cast PMMA which can be burned in both directions the usual index for downward burning is $0.174\pm.001$, but for upward burning the index is only $0.151\pm.004$.

5. Some Comments on Flame Appearance

Although there are certain similarities in appearance of candle-like flames for many different materials, there is also a wide variation in the detailed characteristics. Some samples are topped by a quiescent dome of clear liquid showing no formation of gaseous pyrolysis products below the surface; others show extensive bubbling in the interior. Some samples burn without char or soot formation; some generate much char and soot—and the appearance of the chars differs. Some chars are lacy and stand upright in the flame; others are massive (polycarbonates) and enclose considerable partially reacted polymer. The latter are prone to topple and fall down along the unburned sample as it softens below the char.

Some flames burn quietly; others very erratically as bubbles of fuel gases burst out through the burning surface in an unpredictable manner.

Some polymers melt and drip badly. The melt may run down and refreeze on the sides of the unburned sample; in this way heat is removed from the flame zone and results in an oxygen index higher than that for a chemically similar but non-melting sample. A high molecular weight polypropylene (Hercules Profax 6505) burns with an oxygen index of 0.174; a low molecular weight polypropylene (Epolene N15) has an index of ≈ 0.23. The latter burns with a light blue flame which rides down the specimen on a
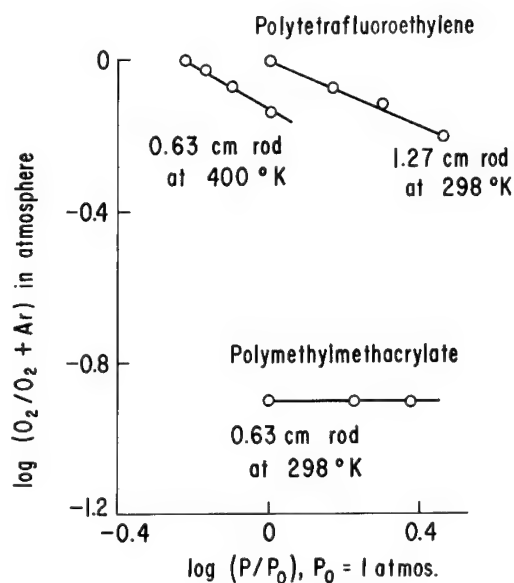
FIGURE 7. *Effect of pressure.*

wave of molten polymer leaving the center standing unburned. Its high index reflects the extra heat loss due to easy melting. When the same material is made into a candle with a ceramic wick and burned off the wick, the index is only 0.177±.005. Some materials melt and run so badly that it is not experimentally possible to measure an index; polyethylene film is an example. Fortunately there are not too many of these.

As the oxygen content of the atmosphere is reduced gradually below the critical level, the flames of many polymers which burn without solid residues (such as polyethylene, polymethylmethacrylate, polyoxymethylene and polytetrafluoroethylene) slowly shrink and the leading edge recedes until just before extinction only a small blue cap exists above the sample. For other polymers, particularly some containing antimony oxide (Sb_2O_3) plus halogen, only large flames are stable. As the oxygen is reduced, a violent flicker appears. It looks as though the flame is suddenly blown back from the leading edge, then jumps forward again momentarily but cannot stabilize itself and the phenomenon repeats rapidly through many cycles until finally the flame although still large is blown off completely. The details of the phenomenon are not understood.

When one considers the great variations in flame behavior, it is rather amazing and gratifying that reproducible indices can be determined for so many different materials.

6. Modes of Inhibiting Polymer Flammability

Having reviewed the characteristics of candle-like flames, we will now discuss their use as a tool to study the burning process. In particular we will be interested in ways to make polymers more resistant to burning in air.

In the simple candle-like model, heat flux from the flame to the condensed phase is sufficient to gasify the polymer at a rate adequate to maintain the flame. If the polymer is modified to require a greater heat flux in order to provide the same flow and quality of fuel gases, a higher flame temperature is required; it is achieved by reduction of the quantity of inert gas in the atmosphere and hence in an increase in the oxygen index.

Likewise if the polymer is modified to yield species in the fuel gases which retard or poison the flame reactions, a higher flame temperature is required to maintain the flame in the face of unavoidable heat losses; in this case too, the higher flame temperature would be achieved by reducing the N_2/O_2 ratio in the atmosphere and thereby increasing the oxygen index.

These two modes of inhibition should be distinguishable. An inhibitor that reacts with the condensed phase to alter the pyrolysis reactions would not be expected to be equally effective in all polymers, since they differ widely in their chemistry; but, in those polymers where it is effective, it should work independently of the nature of the flame

reactions. It should inhibit when the polymer is burned in another oxidant than oxygen, for example, N_2O. This is so because only heat is required from the flame. It will be shown below that phosphorus compounds in epoxy inhibit in this way.

On the other hand, the chemistry in the flame zones of different polymers burning in nitrogen/oxygen mixtures is often quite similar; and an inhibitor which poisons the flame reactions would be expected to work about equally well in polymers of different types, although there appear to be some exceptions. As discussed below, bromine or bromine compounds inhibit in a wide variety of fuels and, therefore, we believe they poison the flame reactions.

However, the flame chemistry can be readily altered by using another gaseous oxidant such as N_2O. Then the nitrous oxide index is defined to be the volume fraction of N_2O in the atmosphere required to sustain steady downward flame propagation under the same conditions specified for the oxygen index. It is a measure of flammability in N_2O/N_2 mixtures. Inhibition in O_2/N_2, but not in N_2O/N_2 flames as measured by relative changes in the oxygen and nitrous oxide indices would indicate poisoning of the flame reactions.

We will summarize briefly the conclusions reached about the mode of inhibition by several classes of inhibitors.

7. Phosphorous Compounds

Phosphorus compounds inhibit weakly in polyethylene (see figure 8 and references [1, 7]); but triphenyl phosphine inhibits strongly in epoxy as

FIGURE 8. *Phosphorus or antimony compounds added to polyethylene (Marlex 5002) without halogen.*

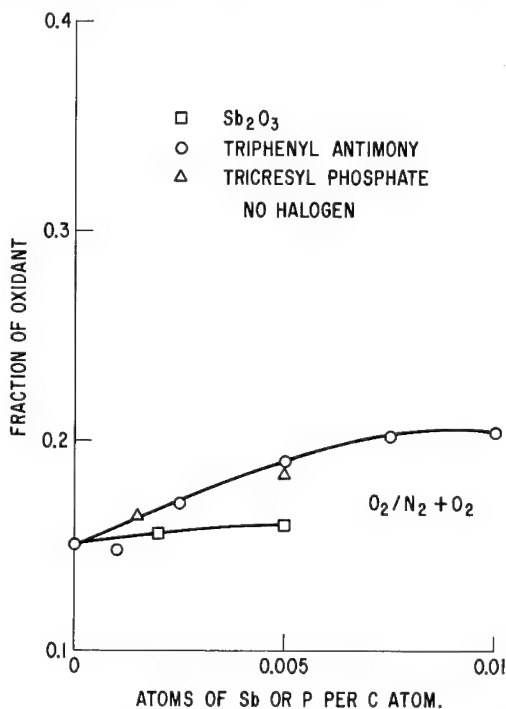

FIGURE 8. *Phosphorus or antimony compounds added to polyethylene (Marlex 5002) without halogen.*
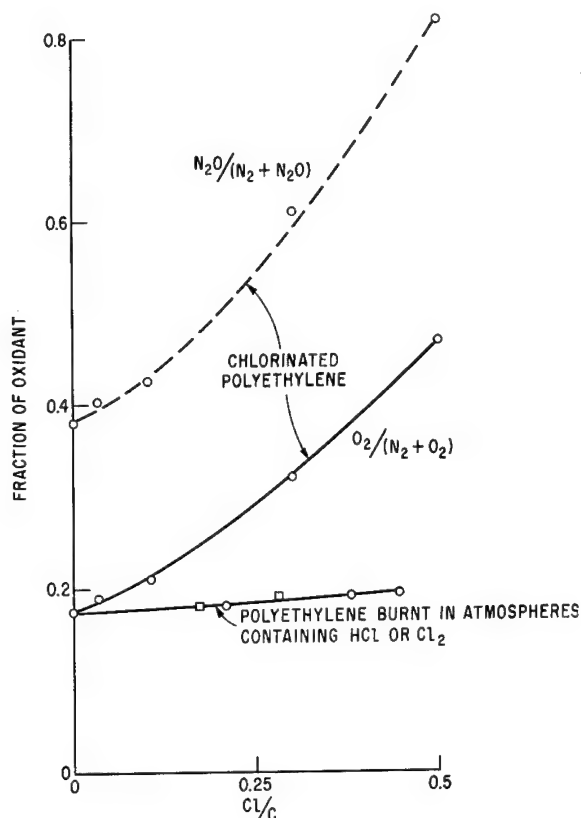
165

FIGURE 9. *Inhibition by chlorine in chlorinated polyethylene.*

shown in figure 10. Furthermore triphenyl phosphine in epoxy is effective for burning both in oxygen and in nitrous oxide; therefore we conclude that it inhibits primarily by affecting the pyrolysis reactions in the condensed phase.

8. Chlorine Compounds

Oxygen and nitrous oxide indices for chlorinated polyethylenes are shown in figure 9. Inhibition is effective in both oxidants and therefore probably does not involve poisoning of the flame reactions. This is consistent with the observation that addition of large amounts of Cl_2 or HCl to N_2/O_2 atmospheres only slightly increase the oxygen index for poly-ethylene as shown by the bottom curve in figure 9.

Gas samples collected just above the burning surface of chlorinated polyethylene contain no molecular oxygen, no chlorinated hydrocarbon, but more benzene and acetylene the greater the degree of chlorination of the polyethylene. (In all cases about 70 percent of the C atoms formed CO and CO_2.)

The chlorinated polyether, penton, and chlorinated polyethylene having the same Cl/C ratio of 0.4 have quite different oxygen indices—namely 0.23 and 0.39 respectively. In contrast to chlorinated poly-ethylene, Penton yielded some chlorinated hydro-carbons in the products.

Thus, all the evidence indicates that Cl compounds

inhibit in the condensed phase by affecting the pyrolysis reactions.

Flames of chlorine-containing samples are sooty and form much char, which may tend to insulate the condensed phase from the flame. Whether or not this effect is important is not known.

9. Bromine Compounds

For *n*-hexane, polyethylene and for epoxy resin the addition of bromine or bromine compounds to a like Br/C ratio results in each case in about the same fractional increase in the oxygen index. This similar effect for quite different fuels indicates that bromine acts primarily as a flame poison.

10. Antimony Compounds

The oxygen index of partly chlorinated poly-ethylene or of polyethylene containing bromine compounds is markedly increased by the addition of antimony in the form of Sb_2O_3 or as triphenyl stibine; but no increase is observed in the nitrous oxide index.

Analysis of the residues from partly burned samples show that antimony is only effective when it vaporizes into the flame, and then only when the oxidant is oxygen. Thus, we conclude that antimony compounds yield flame poisons [7].
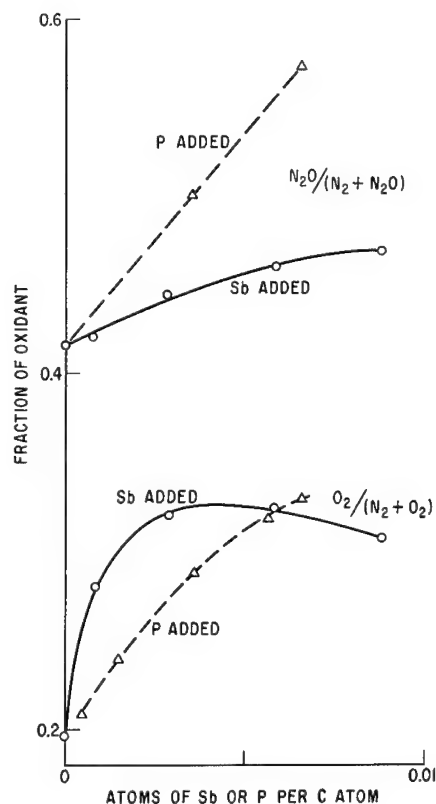

FIGURE. 10. *Triphenyl phosphorus or triphenyl antimony added to epoxy containing no halogen.*

Epoxy same as in table 1.

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It should be noted that phosphorus kills the antimony-halogen synergism in polyethylene by preventing the vaporization of antimony.

Antimony may be added in the form of the triphenyl compound in the absence of halogen. When added in this manner to polyethylene (no halogen) the effect is small as shown in figure 8; the maximum increase in the oxygen index is 15 percent. However, when added to halogen-free epoxy, a large inhibition is observed for burning in oxygen/nitrogen atmospheres, but much less in nitrous oxide/nitrogen. The maximum increase in oxygen index is 66 percent, but only 13 percent for the nitrous oxide index. Again the evidence indicates that the antimony mainly poisons the flame reactions. Here is a case where a flame poison is not equally effective in different polymers, i.e., polyethylene versus epoxy. The implication is that triphenyl stibine vaporizes from the burning epoxy without the aid of halogen, but not from burning polyethylene.

11. Inhibition by Fillers

Inorganic fillers accumulate at the burning surface and appear to smother the flame by interfering with the heat flux to the polymer. At high enough oxygen levels, the cap of accumulated residue will split open or be tipped off to one side, and the flame will flare up until depressed again by the formation of another residue cap. Despite the cyclical character of the burning, it is often possible to determine a reproducible oxygen index; it is usually but not always higher than for the unfilled polymer.

With larger proportions of filler a standing ash may be formed which roughly maintains the shape of the original sample; steady burning is generally observed in these situations; and heterogeneous reactions may be important or even predominant.

In figure 11 it is seen that inert fillers of alumina (or quartz) at high concentrations in epoxy may raise the oxygen index by as much as 40 percent; but the effect levels off and does not continue as more filler is added. On the other hand, at concentrations greater than 40 weight percent, hydrated alumina continues to show a steadily increasing oxygen index; at 60 weight percent $Al_2O_3 \cdot 3H_2O$, the index is twice that of the unfilled epoxy. The nitrous oxide index behaves similarly [6]. The effect presumably arises from heat absorbed in the partial dehydration of $Al_2O_3 \cdot 3H_2O$. Since the effect is observed in both oxygen and nitrous oxide atmospheres, it probably does not involve gas phase reactions with the oxidant. Very small amounts of soot and char are formed.

12. Concluding Comments

If the above discussion is correct, we conclude that simple candle-burning experiments in controlled oxidizing atmospheres can often establish the mode of inhibition and the optimum quantity of chemical additives for burning under these conditions. Appropriate analysis can sometimes be made to check these conclusions.

Of course, it would be nice to know more. However, this will involve a greatly expanded knowledge of the details of pyrolysis reactions at and below the burning surface and knowledge of the complex flame reactions. These are difficult but challenging areas.

In another direction we need to understand better the relationship between the indices observed for candle-like burning and other measures of flammability. Hopefully such knowledge will lead eventually to improved design criteria to control flammability in complex structures.

FIGURE 11. *Inhibition by fillers in epoxy resin.*

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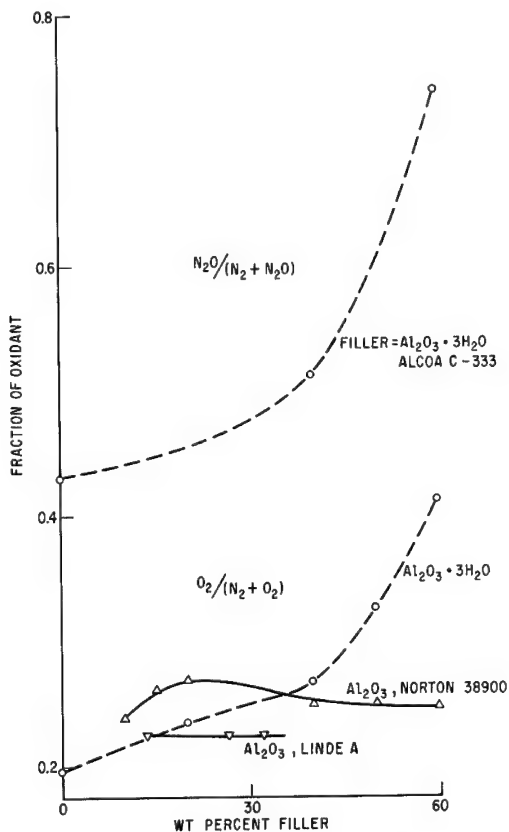[10] C. E. Mellish and J. W. Linnett, Fourth Symposium (International) on Combustion, p. 413. Wilkins & Wilkins: Baltimore (1953).
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Discussion

Raymond R. (Hooker Research Center):

The conclusion in Dr. Fenimore and Dr. Martin's paper that fire retardant inhibition in the condensed phase should be independent of the oxidizing medium implies an assumption that any interactions between the hot molten surface of the polymer and the oxidizing gas are unimportant or unchanged by a change in oxidant. Can you comment upon the validity of this assumption?

Is the temperature profile of the N_2O–N_2 flame the same as that observed with the O_2–N_2 flame?

What are the carbon dioxide and carbon monoxide concentrations on the surface of burning polyethylene? Do they change in the presence of fire retardant additives?

F. J. Martin:

1. The simple candle-like model postulates no direct reaction between the polymer surface and the oxidizing gas; reaction at the surface occurs as a result of heating in a local atmosphere of pyrolysis products and combustion products. Furthermore, it is assumed that reactions between the combustion products and the condensed phase do not significantly influence the pyrolysis reactions at the surface. The question is, "Is this a valid model for actual situations?"

For many polymers burning in oxygen or nitrous oxide mixed with an inert gas, we believe the simple model is valid. Analyses of gases above polymethylmethacrylate, polyethylene, and polyoxymethylene burning at a reduced pressure (6 cm of Hg) in argon/oxygen, 80/20 gave compositions expected for pyrolysis reactions in an inert atmosphere. Furthermore, the heat flux into the polymer, estimated from the measured temperature gradient above the regressing surface, was that required to warm and gasify the polymer without the necessity of surface reactions with any product species (Ref. 7).

Presumably the validity in these cases arises from the similar inert products (primarily H_2O, CO_2, and CO) found above the pyrolyzing surface. If one were to choose an oxidant yielding widely different combustion products (such as F_2 producing HF, CF_4, etc.), the inertness of the products with respect to the polymer-surface pyrolysis reactions would have to be established. Even if one were to add increasing amounts of inhibitor to a polymer, like samples of which were then burned in two different oxidants chosen such that for one oxidant there was no surface-product interaction and for the second there was reaction, comparable inhibition in both oxidants as measured by changes in the suitable oxidant index would be evidence for probable action

in the condensed phase either by a strictly thermal pyrolysis or surface interaction with products; it would not be possible to distinguish these two possibilities by this test alone. (Of course we have not here ruled out the possibility, although it seems remote, that the added inhibitor might be equally effective in both oxidants as a poison for the gas-phase flame reactions.) We have not tried this experiment.

2. Although temperature profiles above polymers burning in N_2O–N_2 mixtures have not been measured, we anticipate that they would be similar to those for burning in O_2 mixtures.

3. The fractions of carbon measured as CO_2 and CO in gas samples collected 0.1 cm above chlorinated polyethylenes burning in Ar/O_2 mixtures at 15 cm of Hg are as follows (Ref. 7):

Polymer Composition	Fraction of C as	
	CO_2	CO
Polyethylene, C_2H_4	0.38	0.30
Chlorinated to $C_2H_{3.8}Cl_{0.2}$	.42	.27
Chlorinated to $C_2H_{3.4}Cl_{0.6}$	.50	.20

With chlorine incorporated into the polymer chain, it is seen that the fraction of carbon appearing as oxides remains nearly constant at around 0.69 at least until the Cl/C atom ratio is increased to 0.3; with increasing Cl, the fraction appearing as CO_2 increases at the expense of the CO. At the same time, the fractions appearing as C_2H_2 and benzene increase.

We do not have such data on other inhibitors in polyethylene.

Robert F. McAlevy, III (Stevens Institute of Technology):

Although the "oxygen index" represents a convenient means of ordering some aspects of polymer combustion it does not appear to be sufficiently fundamental to relate it to the actual mechanisms of ignition, flame spreading and burning of polymers. These will have to be studied individually, and in depth, before a rational "inflammability index" can be evolved. The commentor's laboratory is engaged in these fundamental studies and copies of reports dealing with this work are available.

F. J. Martin:

Certainly much work needs to be done to elucidate the complex processes of ignition and burning. Only

time will tell whether or not the oxygen index will prove to be a useful and meaningful tool in this difficult field.

William C. Kuryla (Union Carbide Corporation):

Dr. Martin in his excellent paper on the burning of polymers, particularly as measured by the oxygen index apparatus, noted on page 168 of the preprint that: "phosphorus kills the antimony-halogen synergism in polyethylene by preventing the vaporization of antimony". Has this been noted for any other class of polymers, and if so to what degree? I believe this is a *very* important observation in that one can easily envision a formulator thinking to himself: "I'll make this article *really* flame retardant by not only putting in the usual antimony/halogen components, but I'll throw in some phosphorus flame retardant as well!"

F. J. Martin:

We have not studied other polymers to see whether or not phosphorus kills the antimony-halogen synergism in them as it does in polyethylene. It would not be surprising to find similar behavior in other materials. This observation points up the desirability of learning more about the chemistry of inhibitor/polymer systems.

Bernard Miller (Textile Research Institute):

The authors mention the desirability of obtaining oxygen index values for the more vigorous upward burning of a sample, which should accentuate the effect of convective heat transfer ahead of the flame front. Our experience agrees with their statement that this kind of experiment generally cannot be carried out with a conventional oxygen index test arrangement. However, we have made what we believe to be related measurements by arranging for the gas mixtures to flow in the reverse direction (down the test chamber) while still burning the test sample from the top. Thus, all products of combustion should be moved ahead of the flame. The resultant data, for textile fabrics, have proven to be quite interesting. Instead of the expected straightforward decrease in O.I. as described by the authors for cast PMMA, we have observed a variety of O.I. changes that are dependent on the gas flow rate. Using about the recommended flow rate (actually 4.8 cm/sec) we have found that downward gas flow often gave a higher O.I. than upward flow, viz:

Material	Upward flow O.I.	Downward flow O.I.
Cotton	0.180	0.186
Acrylic	.182	.188
Wool	.252	.259
Cotton + 3.6% (NH$_4$)$_2$HPO$_4$	.228	.244
Polyester + 5.4% tris-(dibromopropyl) phosphate	.238	.265

In contrast, nylon and polyester have the same index for gas flow in either direction, but in no case have we found a decrease in O.I. with a downward gas flow of 4.8 cm/s.

As stated by the authors, the normal O.I. value is independent of flow rate over the range 3–12 cm/sec, but this is not the case for the reverse flow. At twice the previously mentioned rate, all except two of the above materials recovered their conventional O.I. values. Wool dropped down to 0.246, while the treated cotton (+DAP) was still high at 0.236. So that only in one instance (wool at 9.6 cm/sec downward gas flow) have we observed a decrease in O.I. that could possibly be attributed to increased convective heat transfer. Instead it seems likely that the burning of most of these materials is inhibited by the generation of non-combustible gaseous by-products which are not removed by the lower velocity downward gas stream as they are at higher flow rates or when the gas is moving in opposition to the flame.

The question does arise as to how we can reconcile the above observations with the indisputable fact that materials do burn faster upward than downward. If we remind ourselves that in a reverse flow experiment, the flame itself is still forming above the burning line, we must see that this is not the same situation as in upward burning where the flaming region actually impinges on the unburned portion. The reverse flow experiments do indicate that convective heat transfer itself may not have a significant influence on burning. This would be consistent with other experimental results we have obtained showing that the flame propagation rate for such materials does not change as the flame movement direction varies from horizontal to the candle-like, downward burning mode. In other words, once the flame itself cannot actually come in contact with the material to be burned, heat transfer from it is not consequential.

The reverse flow experiments also are useful in revealing the relative flame quenching capabilities of any non-combustible byproducts. Of the examples given, the most extreme case is the treated cotton, which has a higher O.I. even at the increased downward flow rates. Nylon and polyester, on the other hand, are not affected by gas flow changes.

F. J. Martin:

The downward airflow over a specimen burning at the top end can result in complex gas flows in the flame region where buoyancy becomes important. We have not tried to analyze such flows; rather we have sought to establish a reproducible, easily-obtained flow pattern and defined the oxygen index to apply to it.

One could define some other set of experimental conditions as proposed by Miller, but there appears to be little advantage.

Furthermore, we have sought to interpret our indices in terms of a very simple model for the burning process. Such a model cannot explain

details of the complex flame stabilization process, but can be used to distinguish some interesting differences in burning characteristics of different materials. While Mr. Miller's explanation of flame quenching by "noncombustible byproducts" may seem quite plausible, a much more detailed analysis of the flame would be required to justify it.

C. F. Cullis (The City University, London):

The "oxygen index" method for the measurement of polymer flammability, developed by Dr. Fenimore and Dr. Martin, is proving to be of considerable value. Apart from the determination of the readiness with which flame is sustained at the surface of a burning polymer, however, it is important also to be able to measure the ease of ignition of polymers. Mr. A. W. Benbow has been attempting, at the City University, to determine, by means of an electric arc method, the energy required for ignition of various polymers. Due to the large excess voltage needed to produce an arc, this method is not very satisfactory and experiments are now therefore being carried out which involve measuring the time taken to ignite polymers by means of a hydrogen flame source placed at a given distance above the surface of the polymer.

One of the associated advantages of the "oxygen index" method is that it makes it possible to distinguish between some of the several mechanisms whereby additives confer flame retardance on polymers. Thus, certain additives decrease the rate of evolution of flammable degradation products, while others inhibit the subsequent combustion of these products. Dr. Fenimore and Dr. Martin have shown that these two broad modes of action can be dis-

tinguished by determining whether the inhibiting effect is dependent on polymer structure on the one hand and on the nature of the gaseous oxidant on the other. It is necessary to recognise, however, that flame extinction may be brought about in several ways. Thus the additive may cause the release into the gas phase of a compound which reacts with highly active free radicals, replacing them by less reactive ones [1]. In some systems finely divided solid particles may be given off which catalyse chain-termination processes [2]. In other cases, however, the additive may simply yield a heavy inert gas which "smothers" the flame by reducing the supply of gaseous oxidant; this seems to be the principal mode of action of certain halophosphorus esters [3]. It seems important to be able to devise experimental criteria by which these different modes of action of flame-inhibiting additives may be distinguished.

There are, of course, as Dr. Fenimore and Dr. Martin point out, several other ways in which compounds can exert a flame-retardant action. Thus certain additives (inert fillers) simply act as a heat sink, while others facilitate melting of the polymer [4] or cause the formation of a protective layer of solid which tends to prevent the oxidant from reaching the polymer surface.

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Pyrolysis and Combustion of Cellulosic Materials

Raymond Alger

Naval Ordnance Laboratory, Silver Spring, Md. 20910

Despite centuries of experience with burning cellulosic materials, men still do not agree on the interpretation of their observations. These divergencies of opinion generally involve mechanisms at the microscopic level where areas of ignorance still abound. This review deals with some of these opinions and the supporting experimental evidence pertinent to three chronologically related areas of fire research; namely, pyrolysis, ignition, and fire spread. Some of the ignition concepts and the models for fire spread are not limited to cellulose but should apply to a variety of solids.

Key words: Burning of polymers; cellulose; combustion of polymers; decomposition; fire spread; ignition.

1. Introduction

In the biblical account of a cellulose ignition experiment conducted by Elijah and the prophets of Baal, the outcome was unique in the annals of fire research.[1] First the results conclusively established the source of ignition beyond all doubt and second, the dissenting voices were silenced forever. In contrast, present day fire research generally approaches the resolution of divergent viewpoints and theories through a slow amassing of evidence, not by design but for lack of a quick definitive experiment. Usually, the complexity of the problem permits the results to be rationalized within the bounds of several competing fire models and theories. This paper is concerned with three such problem areas in cellulose fires. The order of presentation follows the chronological development of a fire commencing with pyrolysis and progressing through ignition and fire spread. The scope is limited to small areas where recent results are stimulating new concepts or are providing support for one of the competing models. Our interest is to stimulate and encourage further work aimed at answering a few questions rather than to attempt a general review of cellulose pyrolysis and combustion.

In order to clarify the points of contention and areas of ignorance, it is profitable to outline some of the physical and chemical properties of the fuel and to describe the pertinent characteristics of the fire. The first two sections contain this background information, while the last three parts deal with the new results in support of the various theories.

2. Chemical and Physical Properties of the Fuel

The "ideal" cellulose is composed of anhydro-glucose or beta-glucopyranose structural units $(C_6H_{10}O_5)$ that join together through the 1,4 glucosidic linkages as shown in figure 1 to form a linear molecule. Any number of units odd or even and ranging up to 5,000 or more can unite to form the cellulose chain. The number or degree of polymerization (D.P.) provides a basis for classifying cellulose. Alpha-cellulose consists of the longest chains, i.e., 96 percent of a good grade of alpha-cellulose will have a D.P. in excess of 1,000 based on viscosity measurements (Ott and Spurlin–1954). The boundary between alpha- and beta-cellulose corresponds to a D.P. of about 200 and gamma-cellulose has the shortest molecules, i.e., D.P. up to about 10. Although these categories were initially based on solubilities in a caustic soda solution[2] the boundaries indicate changes in other properties as well. For example, mechanical strength is associated with long chains and this strength is lost when the D.P. is as low as found in the beta- and gamma-cellulose.

The starting material in the experiments described here is alpha-cellulose. Since some of the molecular bonds will be broken during pyrolysis, the weakest links are important in determining the course of events. The C–O bonds are weaker than the C–C bonds, therefore the principal candidates for scission are the A, B, C, and D linkages in figure 1, (Shafizadeh–1969) (Madorsky–1964). Rupture of the bonds in the ring structure (A, B) leads to decomposition of the molecule to yield water, carbon dioxide, carbon monoxide, and char, whereas cleavage of the C or D bonds leads to depolymerization and the production of levoglucosan.

In the next stage of aggregation, cellulose molecules group themselves together to form fibers whose detailed structure remains a point of debate. X-ray diffraction patterns of these fibers indicate ordered

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[1] I Kings, 18.

[2] Beta- and gamma-cellulose are soluble in 17.5 percent NaOH solution but alpha-cellulose is not.
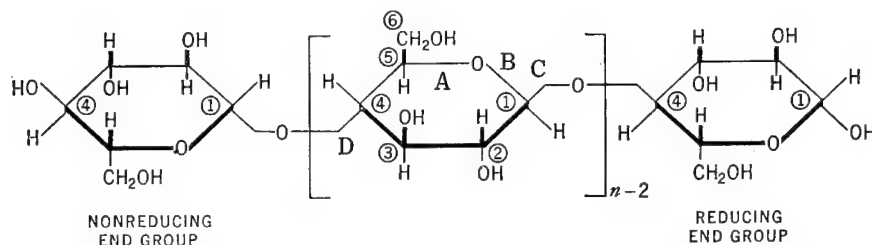
FIGURE 1. *Cellolose chain structure and the anhydroglucose unit (Ott and Spurlin—1954)*

regions typical of a crystalline structure along with disordered regions which are considered to be amorphous. Presumably the forces that hold the molecules together, i.e., cross linking hydrogen bonds and van der Walls attraction are most effective in the crystalline regions. Several types of evidence have been used to indicate the relative magnitude of the crystalline and the amorphous regions, for example:

1. Chemical reactions involving a selective reagent that cannot penetrate the crystal regions of the fiber.
2. Kinetic methods where the observed parameter exhibits an initial rapid rate followed by a slower final rate characteristics of the amorphous and crystalline regions respectively.
3. Physical methods such as the relative intensities of the amorphous and crystalline portions of the X-ray diffraction pattern (Ott and Spurlin–1954), i.e., the crystallinity index CrI defined as

$$CrI = \frac{I002 - Iam}{I002} \times 100$$

where I002 equals the maximum intensity of the lattice defraction in arbitrary units and Iam is the intensity of the amorphous background defraction in the same units (Parker and Lipska–1969).

Both methods 2 and 3 play an important role in the supporting evidence for the pyrolysis models to be discussed later. While the absolute degree of crystallinity values obtained in the various techniques cannot be readily compared, the relative values are in general agreement and provide a useful means of checking the microscopic behavior of the fibers. Typical values of the percent crystallinity ranged from 60 to 90 depending on the source of the cellulose and the measuring technique (Ott and Spurlin–1954).

Crystal sizes and shapes have been studied with the electron microscope and by viscosity measurements of dissolved samples. Typical lengths range from 100 to 300 D.P. depending on the source of cellulose and the treatment. If the length of an anhydroglucose unit is 5.15 angstroms, these crystals would range from about 500 to 1500 angstroms in length and perhaps 40 to 100 angstroms in width (Ott and Spurlin–1954). Since most of the individual alpha-cellulose molecules are at least

5,000 angstroms in length, i.e., D.P. of over 1,000, they can extend through a number of amorphous and crystalline regions. Numerous authors, for example, (Ott and Spurlin–1954, Rebenfeld–1965, Warwicker et al., Manley–1965, and Parker and Lipska–1969) have discussed the various models for describing the crystalline-amorphous structure in cellulose fibers, e.g., micellar theory, the fringed micellar structure, the fringed fibrillar structure, and the folded chain. Fortunately, variations in these models are not crucial to the present state of the pyrolysis models. All of the fiber structures permit bond rupture and molecular rearrangement to occur more readily in the amorphous regions.

3. Stages in Fire Development

3.1. Pyrolysis

When cellulose is pyrolyzed, the principal points of interest are:

1. The identity of the pyrolysis products
2. Their rate of production
3. The dependence of species and yield on heating rate and temperature, and
4. The controlling reactions.

Considerable information and agreement exist with regard to the first three points, but diverging concepts about the mechanisms are one of the principal concerns of this paper. During pyrolysis, cellulose undergoes some very obvious and well known physical changes, e.g., the color changes from white to brown then black, the size and weight are reduced, and the flexibility and mechanical strength are lost. The time and temperature dependence of the weight loss during pyrolysis has been studied extensively and the results constitute one of the principal bits of information regarding the mechanism. Figure 2 shows typical isothermal weight loss curves for two temperatures that bracket the region of immediate concern. Conjecture about the order of the reaction during pyrolysis, i.e., first order, zero order, etc., is based largely on the shape of such curves and the associated measurements of the remaining glucosan. We will return to this point.

If pyrolysis is continued at the temperatures of figure 2, the weight loss eventually reaches about 80 percent and the remaining cellulose has been converted to a char. Very prolonged heating or exposure to higher temperatures, e.g., 600 °C will reduce the char fraction to about 9 percent of the
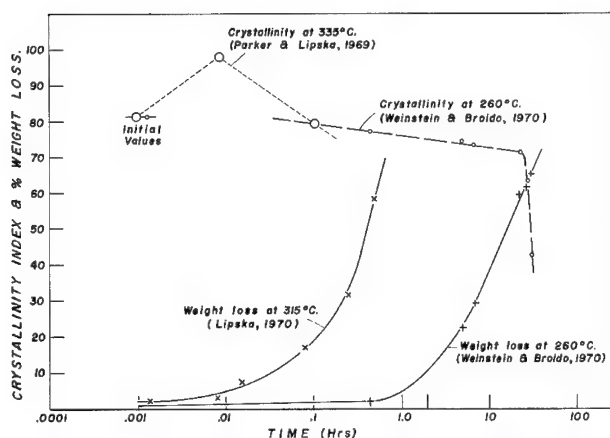
FIGURE 2. *Degree of crystallinity and weight loss as a function of pyrolysis time for several different temperatures.*

original cellulose weight. If the crystallinity is measured throughout the course of pyrolysis, the index will follow the second set of curves in figure 2. The index may be increased slightly during the early stages, but for the most part there is very little change in crystallinity until the weight loss reaches about 50 percent. When the crystallinity shows an increase, it is because Iam for the amorphous region has been reduced and not because of an increase in the reflections from the crystalline portions of the fiber.

The chemistry of pyrolysis is sufficiently complex that the available information consists primarily of a knowledge about the starting material, the stable end products, and how some of these products depend on the thermal treatment. For convenience, the final products have been divided into three categories:

1. Volatile products of molecular weight below about 105. These products escape readily during pyrolysis and at last 59 different compounds have been observed, of which 37 have been identified. Typical examples are carbon monoxide, carbon dioxide, water, acetol, furfural, and a variety of unsaturated aldehydes and ketons.
2. Tar constituents of higher molecular weight. Levoglucosan is one of the principal components, and
3. Chars.

The intermediate char corresponding to the 80 percent weight loss has an approximate formula $C_3H_4O_2$ which is only slightly carbon enriched over the original material. Further pyrolysis to the final 9 percent char involves the elimination of water to give a composition of about 90 percent carbon, 2.7 percent oxygen, and 5.4 percent hydrogen, i.e., a 48 percent increase in the carbon fraction (Parker and Lipska—1969). In a further effort at classification the degradation reactions responsible for product categories 1 and 3 have been termed dehydration or char forming reactions, while the tars are generated in depolymerization processes. Obviously considerable bond rupture and rearrangement are required to achieve the wide variety of products observed. The

distribution of products depends both on the temperature and the temperal position in the course of pyrolysis. At the lower temperatures, dehydration reactions predominate (Martin—1965) while depolymerization with the production of levoglucosan becomes the dominant mode at higher temperatures, e.g., at 360 °C. The ratio of tar/char formation has reached 60/40. Between 275 and 400 °C the pyrolysis products formed appear to be independent of temperature. Under isothermal conditions, all the products are emitted throughout the course of pyrolysis, although not necessarily at a constant rate or ratio (Lipska and Wodley—1969).

Realizing that a reasonably complete understanding of the many reactions and interactions involved in cellulose pyrolysis appears to be a long way off, our principal question is whether a simplified model can account for the general features of pyrolysis, particularly the relative production of volatiles, tars, and chars. Aside from the fundamental interest, the factors controlling the reaction path are of considerable practical interest to the fire community, because most fire retardants for cellulose enhance char production. If we are to intervene either to enhance or suppress combustion, control of the pyrolysis path appears essential.

3.2. Ignition

Ignition in cellulose is similar to other ignitions in the sense that combustion occurs when a suitable combination of fuel, oxygen, and heat are available. Since the fuel concentration is not normally known for pyrolyzing cellulose, ignition conditions have generally been measured in terms of

1. The critical irradiance, i.e., the threshold value of heat input for ignition.
2. The time to ignition for a constant level of heat input, and
3. The ignition temperature which is really the temperature of the surface at ignition.

Both the fuel concentration and the temperature depend on the heating rate, consequently, ignition can occur for various combination of heating rate, temperature, and time. Martin (1965) classified cellulosic ignitions, produced by radiation, into three categories on the basis of the heating rate.

1. Low heating rates where the sample approaches a uniform temperature and the heat losses depend on the local air motion and turbulence,
2. Diffusion controlled ignition which corresponds to intermediate heating rates of 5 to 20 cal cm^{-2} s^{-1}. The temperature profile in the cellulose is determined by the diffusion of heat into the solid, and
3. High heat inputs where the ignition behavior is controlled by the ablation of the irradiated surface.

Furthermore the type of ignition, i.e., transient flaming, sustained flaming, or glowing depends on the fuel supply and therefore the heating rates.

The results discussed here will be limited to the diffusion controlled case where the production of

combustible products is adequate to insure flaming ignition. Two observations (Butler et al.–1956 and Martin [8]–1965) have contributed substantially to our ability to rationalize and predict ignition behavior from the knowledge of the heating rate and the thermal and optical properties of the cellulose sample. First, the time to ignition t_i was found to be inversely proportional to the square of the heating rate, i.e., $t_i \propto \dfrac{1}{H^2}$ where H is the irradiance. Second, a solution to the heat conduction problem for radiant energy entering a semi-infinite slab gave the same inverse relationship provided ignition occurred at a constant surface temperature (T), i.e.,

$$t_i \propto (\Delta T/H)^2 \pi k \rho c.$$

Where $k\rho c$ are the thermal conductivity, density, and specific heat respectively for the slab. Subsequent measurements over the intermediate heating range from 4.4 to 11.6 cal cm^{-2} s^{-1} gave essentially a constant surface temperature of 600 to 650 °C at the time of ignition, (Martin–1965) and (Alvares–1967). With this correlation and despite the lack of a specific ignition mechanism, considerable success has been achieved in predicting ignition conditions for a variety of cellulosic materials.

Efforts to determine the ignition mechanism have concentrated on the pyrolysis products in a search for a species or production rate that could be correlated with the constant ignition temperature. Martin (1965) concluded that a threshold in either the rate or the total yield of the combined combustible products was untenable because at the ignition time both the rate and the amount varied depending on the irradiance, i.e., the rate was proportional to H and the amount to $1/H$. A possibility still under consideration involves an active species that becomes available at the ignition temperature. This concept will be considered subsequently in connection with the recent ignition data. Meanwhile, the principal questions remain: What is the identity of the products responsible for ignition? And what is the controlling reaction?

3.3. Flame Spread

Each successive stage in fire development becomes more complicated to analyze because all of the proceeding stages are involved. In a 1968 review Friedman [12] noted that "Combustion science is not able to specify mathematically the laws governing this process (flame spread) and indeed there is uncertainty as to which variables exert the dominant affects." In addition to a continuing process of pyrolysis and ignition, flame spread also involves heat transfer and aerodynamics. At this point the geometry, size, and orientation of fuel becomes an important factor contributing to the pattern and rate of flame spread. Two examples that illustrate this point are (1) linear flame spread on a card, and (2) exponential fire growth in a box. If a vertical 3×5 card is ignited at the top, flames will spread

downward at a uniform velocity of about $3\frac{1}{2}$ in. per minute (Parker [13]–1969). Other samples ranging from sheets of cotton upholstery to wooden barns 300 ft long have also exhibited constant flame spread rates. All of these cases are geometrically similar, i.e., the fuel is long compared to the cross sectional dimensions. Consequently, only the fuel close to the flame receives heat from the combustion zone. Because of the light fuel loading, the fire quickly consumes the fuel and reaches a fixed size that moves as a narrow band of flames from one end of the fuel element to the other. Most of the combustion heat escapes without contributing to the pyrolysis of unburned fuel.

In contrast, the fire inside a box warms all the inside surfaces. Each segment of surface sees the entire burning volume and the fire spreads in proportion to the burning volume. Again, this behavior has been observed both in small volumes and in full sized houses. Obviously, these characteristics are not limited to cellulose fires. In fact, the linear flame spread behavior has been observed in liquid fires of the proper geometry. However, the details of heat transfer and volatile fuel production are a characteristic unique to each material. For example, the pyrolysis products can influence the heat transfer to unburned fuel by irradiation. In the card experiment, cellulose burns with an almost completely nonluminous flame so that little heat is radiated. The principal objective in flame spread studies has been to simplify the problem by eliminating as many parameters as possible through the choice of sample geometry and orientation so that a solution can be obtained for the heat transfer and aerodynamic affects.

4. Recent Developments in Proposed Mechanisms for the Thermal Decomposition of Cellulose

In conjunction with research on fire retardants, several models have been developed to explain the available cellulose pyrolysis data. These are simple models that seek to determine the principal events that control the production of combustible volatiles and chars; however, no attempt is made to treat the detailed chemical reactions. First we will outline the models and the supporting experimental evidence then examine the points of similarity and divergence. The first model (Parker and Lipska–1969) is for the temperature range between 275 and 360 °C. This limitation is imposed because below 275 °C there appears to be a significant change in the predominant decomposition process, i.e., the rates of dehydration and cross linking becomes competitive with depolymerization. At the higher temperatures, the proposed mechanism is as follows:

1. When pyrolysis commences, thermal vibrations cause the long alpha-cellulose molecules to break at weak links, thereby forming short molecules about 300 to 500 D.P. long. Presumably, the scissions occur primarily in the
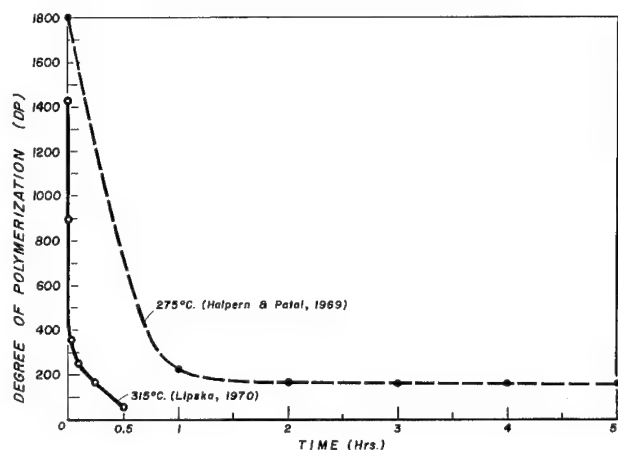
FIGURE 3. *Degree of polymerization as a function of pyrolysis time.*

amorphous regions of the fiber; consequently, the short molecules are mostly in ordered crystalline segments. Evidence of this rapid reduction in size comes from measurements of the degree of polymerization as a function of pyrolysis time. Figure 3 shows typical degree of polymerization characteristics for two pyrolysis temperatures, one above and one at the 275 °C boundary.

2. Next, the short molecules begin to unzip and produce severed monomer units. All of the molecules were assumed to depolymerize simultaneously by starting at one of the ruptured ends and unzipping progressively through the molecule. This concept of simultaneous unzipping is based on two bits of evidence. First at 288 °C the remaining glucosan units in figure 4 decrease linearly with time after the initial rapid adjustment. Second, the weight loss curve exhibits a linear time dependence up to at least 50 percent of the weight loss, i.e., the reaction rate is of zero order. In figure 4 there is an initial 5 to 10 percent decrease in weight which occurs too rapidly to plot on the time scale of this figure. Presumably, the rapid unzipping of molecule ends in the amorphous region is responsible for this sudden change. The crystalline regions are assumed to be more stable and therefore responsible for the subsequent weight loss exhibited in the linear part of the curve.

3. The degradation products formed in this unzipping process can go either into char forming reactions where dehydration liberates CO, CO_2, H_2O, etc., and leaves a residual char or they can undergo a rearrangement to form levoglucosan. While the reaction details are not essential to the development of the model, the yields of levoglucosan and char, i.e., about 60 percent and 40 percent respectively do provide evidence for the two competing processes.

4. When the cellulose is heated with fire retardants two effects are observed. The rate of degradation is enhanced and the yield of char is increased. In the model, the retardant acts in two ways. First, it increases the number of short molecules, thereby increasing the overall rate of unzipping, and, second, it interacts with levoglucosan to generate a furanose derivative which forms char in preference to combustible volatiles. Evidence for these conjectures hinges on measurements of levoglucosan and furanose derivative yields as functions of the fire retardant treatments.

The second model (Weinstein and Broido–1970) is based on isothermal data to 260 °C.

1. Initially the behavior is similar to the first model except that the rapid phase of decomposition becomes constant at a D.P. of about 160 as shown in figure 3. During this constant period the crystallinity index in figure 2 also remains nearly constant.

2. This model is based on competing dehydration and depolymerization reactions, where the results depend on the heating rate and the sample purity. Dehydration is favored by cross links between neighboring units in the crystalline regions. Consequently, the amount of char produced depends on the original amount of order and disorder in the sample. Depolymerization is favored by high temperatures and once started, a molecule is assumed to unzip completely in a time short compared to the pyrolysis period. Presumably the number of molecules unzipping at any one time is proportional to the number present and the reaction is assumed to be first order. As the pyrolysis continues the number of cellulose molecules decreases, but the D.P. and crystallinity remain unchanged in agreement with evidence in figures 2 and 3, for the low temperature samples. Other evidence comes from weight
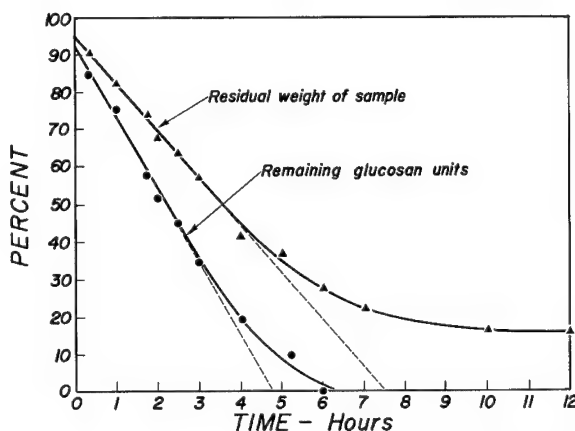

FIGURE 4. *Pyrolysis of alpha-cellulose in nitrogen at 288 °C (Parker and Lipska—1969).*

loss curves where the rates indicate a first order reaction.

3. Fire retardants are assumed to catalyze reactions in the initial stage of bond rupture where they can affect the active ends of molecules to enhance cross linking and thus the char forming reactions.

A slight variation on this model is found in (Halpern and Patai–1969), where the general assumptions are the same regarding the rate of reaction; however, the initial bond ruptures give some crystalline segments about 160 D.P. long and some shorter amorphous segments. Dehydration is assumed to predominate in the amorphous segments leading to char formation, while the crystalline segments favor depolymerization.

A comparison of these models reveals the following points of divergence.

1. The differences commence with the initial rapid segmentation of the fibers. In the first model, the molecules continue to decrease in length, while in the second case, the D.P. remains fixed throughout much of the reaction.
2. The pyrolysis rates lead to different orders for the main portion of the unzipping reaction, i.e., zero order and first order respectively.
3. While unzipping becomes a dominant mechanism at high temperatures, different modes are invoked in the two cases, namely, slow unzipping of all molecules simultaneously versus rapid and complete unzipping of a few reacting molecules.
4. The choice between char and tar forming reactions enters at different stages of degradation and therefore is controlled by different parameters.
5. Finally different modes of intervention by the fire retardant materials are required to meet the difference in the char and tar forming reactions.

In a way, such conflicts are to be expected because each model is trying to explain a different set of experimental data. Furthermore, the experimental conditions, i.e., sample material, temperature, and measuring procedures were sufficiently varied to prevent reliable extrapolations from one to the other. The temperature differences and heating techniques are probably the most influential parameters. For example the temperature effects are very noticeable in the weight loss and glucose loss data. The Parker and Lipska model contains the assumption that these loss curves exhibit three regions of behavior as shown in figure 4, i.e., the initial rapid loss, the linear region corresponding to the simultaneous unzipping of all the molecules, and the final slow approach to the intermediate char. At high temperatures the linear region includes the majority of the weight loss, but at lower temperatures it is not as pronounced. Since the whole curve does not follow zero order kinetics, some attention has been given to the relative degree of fit to the data that can be obtained for the zero order and a first order

curve. In some preliminary efforts to fit the data for temperatures above 275 °F, a computer was programmed to perform two tests, (a) to find the pyrolysis time interval over which zero order and first order curves would fit the data within the same allowed deviation, and (b) to find an exponent for the curve giving the best fit. In the first case, the zero order gave the longest time interval and in the second the exponent was a fraction much closer to zero than unity.

Obviously a first step in resolving the conflict over pyrolysis models involves obtaining compatible data so that all theories are based on the same experimental observations. If the data does not converge when common materials and experimental parameters are employed, it may be necessary to return to Mount Carmel for another decision.

5. Some Recent Ignition Results

For intermediate heating rates the constant ignition temperature gave rise to speculation favoring a threshold for a reactive pyrolysis species as the controlling factor in cellulose ignition. In a series of experiments, Alvares (1967) examined this possibility along with the classical piloted, thermal, and free radical self-ignitions. The fuel and external heating rate were held constant so that the ignition time could be measured as a function of the environment. Both the composition of the atmosphere and the pressure were varied. Presumably, the variations in oxygen concentration at constant pressure did not affect the pyrolysis process prior to ignition. Consequently, the dependence of ignition temperature on the oxygen concentration shown in figure 5 was interpreted as evidence against the reactive product threshold theory. While the results were compatible with the thermal self-ignition model, the qualitative nature of this study did not rigorously exclude the piloted or free radical chain branching mechanisms.

In a recent re-examination of this data, the results were compared to values computed for a simplified and idealized thermal auto-ignition (Alvares and
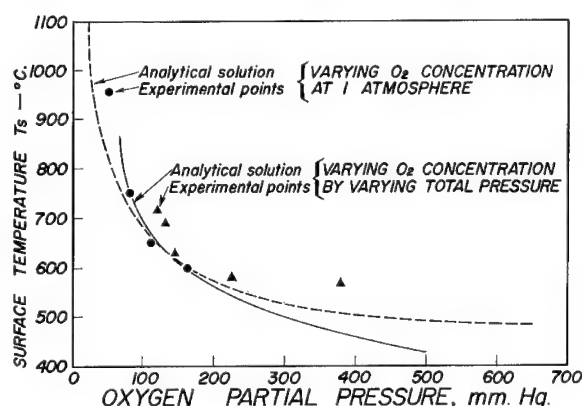

FIGURE 5. *Surface temperature at time of ignition as a function of oxygen partial pressure.*

Martin–1970). Ignition times were computed as functions of pressure, oxygen concentration, and diluent gas composition. In this model, ignition occurs when the heat release rate just exceeds the rate of heat loss. Simplified expressions were developed for the pertinent parameters, e.g., heat loss, reaction rate, and surface temperature. A digital computer provided calculations of ignition times versus total pressure and oxygen partial pressure. Typical results in the form of a calculated curve for ignition temperature versus oxygen pressure are shown in figure 5 along with experimental data points. At the extremes of high and low oxygen concentration, some additional factors become important that were neglected in the simplified model. The high temperatures associated with low oxygen concentrations are not observed because the surface ablates away before such temperatures can be reached. Also the model makes no correction for radiative heat losses at high temperatures. For intermediate oxygen concentrations the calculated values are quite compatible with the experimental points. At high oxygen concentration, the model predicts ignition temperatures below the observed values. Presumably, the minimum ignition temperature corresponds to the onset of sufficient pyrolysis to form a combustible mixture. Fuel production is assumed to be adequate in the simplified model; however, a logical extension would include a term for the kinetics of fuel production. In view of the favorable results obtained with this model, a more sophisticated description of the thermal self-ignition process would appear to be in order.

6. A Simplified Flame Spread Model

The experiments to be described here are submitted as an example of a flame spread geometry that appears to have sufficient simplicity to make it worth a more rigorous treatment. The desired end product should be capable of predicting flame spread velocity from the thermal, chemical, and physical properties of the fuel and atmosphere without resorting to empirical parameters. Downward flame spread along a long thin sheet or card of cellulose fits the criterion for a simple geometry that minimizes the number of parameters entering the balance of energy and fuel transport. The flame spread mechanism proposed by Parker (1969) contains two very important observations. First the pyrolysis gases are released behind the flame front. This is in contrast to the belief that in cellulosic materials the pyrolysis gases are distilled from the surface ahead of the flame front. Second, the heat transfer to the surface is principally by gas phase heat conduction.

These mechanisms are the result of the geometry at the leading edge of the flame. The flame stands away from the surface and extends downward beyond the visibly darkened zone where the pyrolysis products are being generated. The high temperatures in the flame and the close dimensions favor heat conduction in preference to convection and the lack

of a luminous flame minimizes radiation as a source of heat transfer to the unpyrolized material under the flame overhang. In Parker's paper the flame velocity was calculated from physical and thermal characteristics of cellulose, the pyrolysis rate as a function of temperature, and measured values of the overhang and standoff distances. Once the parameters controlling the flame overhang and standoff distance are understood in terms of the fuel and environment these dimensional measurements should no longer be required.

This brief examination of some problems and progress in pyrolysis, ignition, and flame spread shows that there is promise of significant future developments as well as room for another Elijah with his definitive experiments.

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Discussion

J. H. Magill (University of Pittsburgh):

The role of basic and acidic flame retardants leads me to inquire about the efficacy of (1) a chemically bound inhibitor (or retardant) versus (2) the same chemical element or group present as an integral part of the polymer.

Mention was also made (in your paper) about the retardant effect produced through radiation crosslinking cellulose, but nowhere (it seems) has much attention been given to the crystallinity of many of the polymers tested in the Symposium. One would hardly expect a low and high crystallinity polymer to behave similarly if there was an appreciable difference in the enthalpy of fusion. I wish to inquire of Drs. Alger and McAlevy III, if the crystalline state of the polymer is important here. Furthermore, based on the models of Jellinek, figure 10 (p. 106 of preprints), the susceptibility of the structure to attack may be explained on the accessibility of oxygen to the polymer. The nature of the morphology or polymer architecture can be modified experimentally to test if this model is the most relevant.

R. Alger:

In answer to Dr. Magill's questions, we have no data on the retardant efficiency of an inhibitor present on cellulose compared to the same chemical element incorporated in the molecule. Lipska has measured the effect of two halogens on the production of char during the pyrolysis of cellulose. Comparable weights of potassium bromide added to cellulose and iodine substituted in the cellulose molecule produce comparable increases in the yield of char. The second question was concerned with the importance of the crystalline state of the polymer. According to the pyrolysis models for cellulose, the initial bond rupture occurs principally in the amorphous regions. Consequently the degree of crystallinity would influence the initial rapid drop in weight loss, i.e., this initial weight loss should be less for samples of high crystallinity.

D. C. Aldrich (Massachusetts Institute of Technology):

You indicated that the pyrolysis mechanisms for cellulose proposed by various investigators are inconsistent because they are based upon data obtained with different sample material, temperature, measuring procedures and techniques. Would you not also include the differences in sample geometry and cracking behavior of the char structure since these effect secondary pyrolysis and heat convection by the escaping volatiles? You suggested that these discrepancies could be eliminated by choosing a common experimental technique. What technique do you suggest? If an isothermal technique were so chosen, would it be possible to apply the data obtained in this manner to large scale applications?

R. Alger:

In answer to the questions raised by Donald Aldrich, (1) sample geometry, particularly the sample thickness, is an important parameter in attempts to obtain experimental reproducibility, (2) the feasibility of using isothermal pyrolysis data for large scale applications will depend on the particular applications; e.g., the isothermal data can be used in applications involving fire retardant treatments and for the identification of pyrolysis products; however, quantitative yields of products will depend on the particular time temperature schedule.

R. F. McAlevy, III (Stevens Institute of Technology):

The author has ignored much of the standard combustion literature in his survey. Some of the problems that are cited as still outstanding in the case of cellulose have, in fact, been solved for any fuel bed material.

Much of the work was done under the aegis of aerospace research funds, so the examples used to illustrate solutions, and titles of papers, deal with solid propellants.

The mechanism of solid fuel ignition in an oxidant containing environment (air), was understood 10 years ago. (McAlevy, R.F., III, Cowan, P.L., and Summerfield, M., The Mechanism of Ignition of Composite Solid Propellants by Hot Gases. *Progress in Astronautics and Rocketry: Solid Propellant Rocket Research*, Vol. 1, p. 652, Academic Press, 1960.) An excellent review of solid fuel ignition theory was presented a few years ago, "Theory of ignition of solid propellants," Price, E. W., Bradley, H. H., Jr., Dehority, G. L. and Ibiricu, M. M., AIAA J. 4, 1154–1181 (1966).

The mechanism of flame spreading over a solid fuel surface has recently been revealed. Flame Spread Over Fuel Beds: Solid Phase Energy Considerations, Lastrina, F., Magee, R. S., McAlevy, R. F., III, presented at the Thirteenth Symposium (international) on Combustion, Univ. of Utah, Salt Lake City, Utah, Aug. 24–28, 1970; to be published in 1971.

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R. Alger:

Professor McAlevy's point regarding the extensive ignition literature is well made; however, I cannot share his conclusion that the ignition problem is solved for cellulose, at least in sufficient detail to meet current requirements. Much of the rocket ignition work dealt with the problem of comparing gas-phase models to the condensed-phase ignition theory that was prevalent at that time. In the case of cellulose, the competing processes all involve gas-phase reactions. The question is, which species starts the reaction, i.e., radicals, one of the 59 stable pyrolysis products, or catalyst. When the Semenov thermal autoignition theory is applied to the problem, the boundary conditions imposed by the experiment and the criteria for ignition have a strong impact on the solution and the degree of detail that can be accomodated in the expression for the conservation of material and energy. The work of Martin and Alvares was included here because the boundary conditions include cellulose and a fairly common procedure for applying external heat. In other respects, they follow their predecessors by resorting to simplifying assumptions that are quite general. Consequently, the number of fitting parameters introduced to compensate for the dearth of known physical and kinetic constants detracts from the rigor of the results.

An example of such generalization is the criteria for ignition. Martin and Alvares assume ignition occurs when the energy released in the elemental volume exceeds the energy lost. McAlevy, et al., assume ignition occurs when a combustible mixture of pyrolysis products and oxidant develops. Obviously, both of these general conditions must be met, but the details describing how are swallowed up in the fitting parameters. Additional work will be required before detailed boundary conditions such as the production of the various specific pyrolysis products can be incorporated in the autoignition model.

With respect to the mechanism of flame spread over a solid surface, Parker, 1969, deRis 1969, and Lasterina, et al., 1970, have converged upon similar expressions for the spread velocity, at least for a thin fuel element. All the models use gas-phase heat conduction as the principal heat transfer mechanism; however, there are some basic differences in the physical models employed. Parker begins with a detailed study of the flame front and concludes that the flame standoff distance is intimately related to the heat transfer and that pyrolysis occurs behind the flame front following a preheat zone that extends up to the flame front. Although the deRis model extends the flame to the surface, the pyrolysis zone is behind the flame front in agreement with Parker's findings.

R. Friedman (Factory Mutual Research Corporation): (communication)

In regard to the theoretical status of the flame spread process, it seems valuable to call attention to the theories of de Ris [1] for thermally thick and thermally thin materials, which have been remarkably successful without recourse to adjustable parameters. These theories give absolute prediction of spread rate, including dependence on oxygen partial pressure, total pressure, and sample thickness, without requiring knowledge of the chemical rates. The gas phase reactions are assumed to be infinitely fast, once fuel and oxygen have diffusively mixed, and they occur all the way to the surface (i.e., no flame stand-off distance is assumed). Forward heat transfer from the flame through the gas phase to the solid is crucially important for both thin and thick fuels.

It was possible to solve the associated mathematical models, provided one assumes constant density and transport properties and a uniform velocity profile.

The thin-fuel solution for the spread velocity, V, is

$$V \cong \frac{\sqrt{2}\lambda}{\rho_w C_{pw}\tau}\left\{\frac{T_{\text{flame}}-T_{\text{vap}}}{T_{\text{vap}}-T_\infty}\right\}$$

where λ is gas thermal conductivity, τ is fuel half-thickness, and subscript w stands for the solid-phase. Correspondingly, for a thermally thick fuel,

$$V = V_a \frac{\rho C_p \lambda}{\rho_w C_{pw}\lambda_{wy}}\left\{\frac{T_{\text{flame}}-T_{\text{vap}}}{T_{\text{vap}}-T_\infty}\right\}^2$$
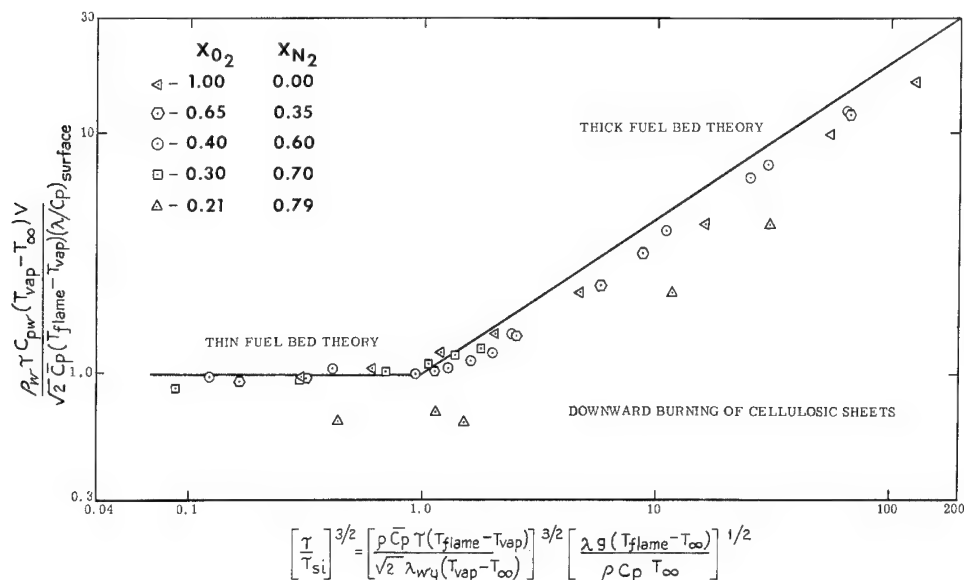
where $V_a \cong [\lambda g(T_{\text{flame}}-T_\infty)/\rho C_p T_\infty]^{1/3}$ is the effective gravitationally-induced gas-phase velocity evaluated one characteristic gas-phase length $2\lambda/(\rho C_p V_a)$ above the fuel bed. λ_{wy} is the fuel bed thermal conductivity normal to the surface.

The thin-fuel formula predicts a spread rate independent of both the opposing gas velocity, V_a and pressure; however the spread rate does increase with the adiabatic stoichiometric flame temperature T_{flame}. The thick fuel bed result is quite different. In this case the spread velocity is proportional to V_a, so that in a quiescent environment with gravity, the spread rate is proportional to the two-thirds power of pressure.

The data taken by Royal and reported by Lastrina et al. [2] are correlated in the accompanying figure. The coordinates are chosen so that both the thin and thick fuel data should correlate if the theories are valid. The ordinate is proportional to the spread velocity while the abscissa is proportional to pressure. The specific choices of property values do not influence the shape of these curves; they influence only the relative positions.

One sees that the correlation is very good for oxygen mole fractions X_{O_2} greater than 21 percent. The data for 21 percent O_2 have the correct shape, but are shifted downward and to the right.

These data lend powerful support to the two theories. This agreement suggests that gas-phase reaction kinetics is unimportant in the range of experimental conditions. One does anticipate, however, that as the pressure or oxygen concentration decreases, an extinction point will be reached, be-

$$\frac{\rho_w \Upsilon C_{pw}(T_{vap}-T_\infty)V}{\sqrt{2}\,\bar{C}_p(T_{flame}-T_{vap})[(\lambda/C_p)]_{surface}}$$

	X_{O_2}	X_{N_2}
◁ –	1.00	0.00
⊙ –	0.65	0.35
⊙ –	0.40	0.60
□ –	0.30	0.70
△ –	0.21	0.79

THICK FUEL BED THEORY

THIN FUEL BED THEORY

DOWNWARD BURNING OF CELLULOSIC SHEETS

$$\left[\frac{\Upsilon}{\Upsilon_{si}}\right]^{3/2} = \left[\frac{\rho\,\bar{C}_p\,\Upsilon(T_{flame}-T_{vap})}{\sqrt{2}\,\lambda_{wg}(T_{vap}-T_\infty)}\right]^{3/2}\left[\frac{\lambda\,g(T_{flame}-T_\infty)}{\rho\,C_p\,T_\infty}\right]^{1/2}$$

cause of reaction kinetics. This extinction point should be sensitive to small concentrations of gas-phase inhibitors.

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Robert H. Barker (Clemson University) (communication):

Mr. Alger has correctly pointed out the importance of the factors controlling cellulose pyrolysis pathways and their relevancy to the problem of fire retardance. Unfortunately the models which he has presented to describe the pyrolysis mechanism are probably not the best description of these factors. Although there are several points where these models do not seem to provide an adequate explanation for experimental observations, the most disturbing to me is the mechanism proposed for levoglucosan formation. This is a particularly important facet of any cellulose pyrolysis model because of its direct bearing on the nature and rate of the chain unzipping reaction and consequently on the rate of formation on the flammable volatiles which serve as fuel for flaming. It is probably at this point that many flame retardants exert their influence.

Mr. Alger expressly states in the first model and implies in the second that the product of the cellulose unzipping is either glucose or some simple glucosan; these monomers then undergo conversion to levoglucosan in some subsequent step. Such a proposal has ample precedent in the older literature but is probably erroneous on several accounts: it does not account for the large variation in products observed when cellulose is pyrolyzed at different temperatures; there is no obvious reason why simple cleavages of glycoside bonds should occur in a systematic sequence as required for unzipping; the conversion of glucose and simple glucosans to levoglucosans is usually a very low yield process whereas high yields are often obtained from cellulose; and, finally, the intermediacy of glucose considerably complicates the mechanisms which must be proposed to accurately describe the action of most flame retardants. Of course, it is generally recognized that mechanistic models are only useful approximations rather than accurate descriptions of real chemical processes, but in this case there is available a great deal of information which would seem to lead to a more useful model.

Numerous proposals have been made in the literature. As early as 1921, Irvine and Oldham [1] proposed that the first step in pyrolysis was hydrolysis to glucose followed by dehydration of the glucose to form levoglucosan. Essentially this same mechanism was proposed again by Heuser [2] in 1944. Similarly, Tamaru [3], in 1951, proposed that the mechanism of cellulose pyrolysis involved depolymerization of the macromolecules to some low molecular weight species. He contended that some of this species underwent dehydration and polymerization with continued and increased heating to yield a high polymeric material, while the remainder of the species underwent further decomposition. The polymeric material was believed to be degassed by heat with resulting aromatization and evolution of carbon monoxide, carbon dioxide, methane, and hydrogen.

Esteve and coworkers [4] believed that depolymerization of cellulose to levoglucosan through scission of 1,4-glycosidic linkages, followed by cyclization to the glucosan occurred during pyrolytic degradations. It was thought that part of the levo-

glucosan polymerized and aromatized to form chars while the remaining levoglucosan underwent destructive distillation to form flammable tars, volatile gases, and water. Ivanov et al. [5], in 1956, independently proposed a similar mechanism by which cellulose pyrolytically degraded in vacuo through splitting of the 1,4-glycosidic linkages with concurrent formation of levoglucosan.

Martin [6] and Day [7, 8] suggested that pyrolytic degradation of cellulose might involve a free radical process; however, neither investigator described his suggested mechanism in detail. Furthermore, they were unable to find evidence to support their postulations although Arthur [9] has recently reported ESR spectral data which may be interpreted as evidence of homolytic degradation. Esteve [4] calculated the energy of activation for the pyrolysis of cellulose and found it to be substantially lower than that required for a free radical process.

Madorsky and coworkers [10], in 1956, proposed a mechanism based upon random dehydration along the cellulose chain occurring simultaneously with scission to produce levoglucosan, water, carbon monoxide, and carbon dioxide. They based this theory on the fact that C–O bonds are thermally less stable than C–C bonds. In 1958, Madorsky refined the theory to involve thermal scission of the C–O linkages between rings, followed by transfer of a hydrogen from the primary alcohol to the oxygen of the broken glycosidic linkage and formation of an oxygen linkage between C–1 and C–6. He deduced that, when a similar scission took place at a point one structural unit removed from that of the original scission, levoglucosan would be formed. Scissions at points more than one unit removed from the original should result in nonvolatile multiple unit chain fragments [11].

Schwenker [12, 13] reasoned that if the pyrolysis of cellulose involves direct depolymerization to levoglucosan, then modifying cellulose at the C–6 positions should minimize levoglucosan formation and decrease flammability. In support of his proposal, he oxidized approximately half of the primary hydroxyls of a cellulose sample and found that when pyrolyzed it yielded only half as much levoglucosan as did the untreated sample. The sample also exhibited reduced flammability.

In 1957, Golova et al. [14] investigated the effects of the packing density of cellulose chains on the pyrolytic decomposition of cellulose in a vacuum. They found untreated cellulose to give approximately 60 percent levoglucosan, while mercerized cellulose yielded only 38 percent, hydrocellulose from cuprammonium solution about 15 percent, cellulose hydrate from unoriented viscose staple about 4 percent and cellulose hydrate from oriented viscose rayon about 5 percent. With this information they concluded that a change in the density of the cellulose chains caused a change in the courses of the chemical processes occurring during pyrolytic decomposition. Decreased packing density was believed to cause a decrease in levoglucosan formation, while increased packing density hindered the side processes

of hydrolysis and dehydration, thus increasing levoglucosan formation.

Golova also investigated the theories which considered levoglucosan to be formed through an intermediate stage in which cellulose was hydrolyzed to glucose and then dehydrated. Golova found that pyrolyzed cellulose gave a levoglucosan yield of 60 percent under vacuum whereas α-b-glucose gave only 5–6 percent. Decreasing the degree of polymerization of cellulose to 150 did not significantly affect the yield of levoglucosan, yet cellobiose was found to yield only 3–4 percent levoglucosan. From these data, Golova et al. [15] concluded that the glucose intermediate theory was incorrect. They further proposed that in regions of high packing density, levoglucosan formation is favored and side reactions are secondary. In regions of different physical structure, dehydration and hydrolysis are the primary reactions with the production of levoglucosan less favored. Based on this information, Golova and coworkers proposed a theory, similar to that later proposed by Madorsky [10], in which levoglucosan was thought to be formed through scission of the 1,4-glycosidic linkages followed by hydrogen abstraction and cyclization to levoglucosan. Further, they concluded that there is some limiting D.P. below which levoglucosan formation is not favored.

In an effort to gain further support of their cellulose pyrolysis theory, Golova et al. [16] degraded cotton cellulose through mild hydrolysis to obtain samples which represented a range of D.P. They thermally degraded the samples at constant temperature for successively increasing time increments and found that all of the samples rapidly degraded to a limiting D.P. of about 200 which remained unchanged during further decomposition. They then concluded that the mechanism of pyrolysis involved initial breakdown to a D.P. of 200, followed by complete depolymerization of the chains yielding levoglucosan. Golova [17] later showed that levoglucosan production was low during the initial stages of pyrolysis and that a large amount of volatile products was produced. In the later stages of pyrolysis the yield of levoglucosan increased and remained constant as degradation continued.

In reporting their work, Golova and coworkers did not speculate on the reason for the apparent stability of the cellulose molecule having a 200 D.P., nor did their results establish whether this number represents an average over a broad spectrum or whether a 200 D.P. was actually a critical size for the cellulose chains. They did surmise the latter. From their observations, it might be further hypothesized that the 200 D.P. represents the average length of the crystalline regions, where chain packing density would be greatest. Thus, one might expect the initial breakdown to be that of the amorphous areas where side reactions would be favored. Breakdown of the amorphous areas could be followed by complete depolymerization of the chains within the crystalline areas, where levoglucosan formation would be favored. This would be consistent with the recent
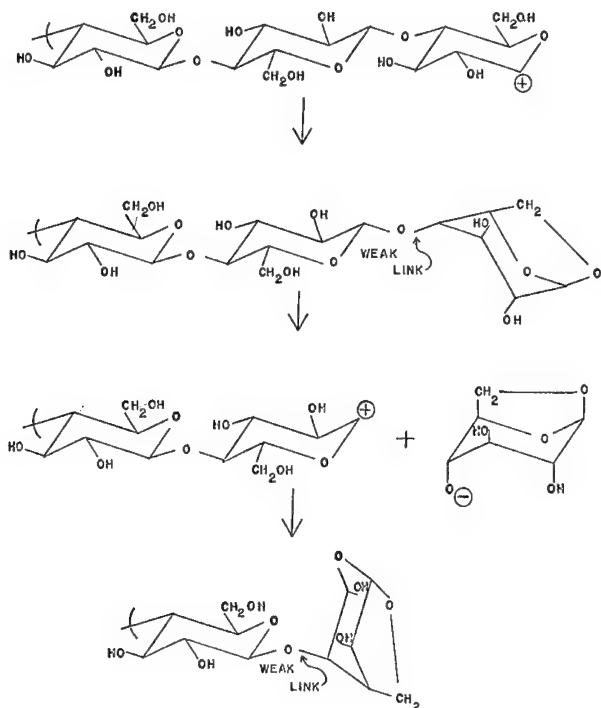
results of Parker and Lipska [18] and Weinstein and Broido [19] which were reported by Mr. Alger.

Honeyman [20] investigated cellulose pyrolysis to gain information applicable to the improvement of flame retardants for cellulose. He pointed out that, in order to form levoglucosan from the anhydroglucose units of the cellulose chain, an interconversion from the all-equatorial C1 to the higher energy, all-axial 1C conformation must occur (see Scheme I). If this process were an integral part of the depolymerization process it would account both for the difference in products observed at various temperatures and the sequential nature of the chain unzipping reaction. Only at higher temperatures would there be sufficient thermal energy for a significant number of the cellulose anhydroglucose units to exist in the strained 1C conformation; thus only at higher temperatures would there be a significant amount of unzipping and levoglucosan formation relative to dehydration, cross-linking, and aromatization. But in those cases where sufficient thermal energy was available for the C1 to 1C interconversion to occur at the reducing end of the cellulose chain, the glysosidic bond joining the terminal unit to the one adjacent to it would be axially disposed relative to the terminal ring and thus subjected to considerable strain. This would weaken the bond and facilitate the cleavage of the terminal unit from the chain. At the same time, the adjacent unit would be converted into a 1,6-anhydro structure with a 1C conformation. Thus the cleavage of each unit from the reducing end of the chain would labilize the next unit for cleavage and produce the observed unzipping reaction.

Mack and Donaldson [21] have recently proposed a mechanism similar to this to explain the reduction

in flammability which they and others have observed from samples of cotton cellulose treated with inorganic bases. They proposed a base-catalyzed degradation below the minimum temperature necessary for the Cl to 1C interconversion. This catalyzed reaction should be in a direction other than that which would produce levoglucosan. We have also proposed a similar explanation for the flame retardant action of certain phosphates in which phosphorylation of the cellulose occurs at C–6 to block the unzipping reaction and inhibit levoglucosan formation. Simultaneously the degradation reactions are assisted so that they occur more rapidly at lower temperatures and thus produce predominently nonflammable gases and char [22]. We have found the efficiency of various classes of flame retardants to correlate with their ability to phosphorylate, crosslink, and catalytically dehydrate cellulose as shown by thermal analysis (23, 24), thermochemical studies [25] and investigations of model substrate reactions [26].

The majority of the investigations of cellulose pyrolysis have been carried out near or below the cellulose combustion temperature but they are probably valid nevertheless. Holmes and Shaw [27] investigated the pyrolysis of different cottons in vacuum and dry air mainly at 418 °C while Berkowitz-Mattuck and Noguchi [28] investigated the effect of one-second exposure of cellulose to high radiant flux levels of 5–25 cal/cm² s. From both investigations it was concluded that the same mechanism observed in lower-temperature pyrolyses operated in these investigations. Reductions in tar formation with increased char yields were reported to be the resultant effects of flame retardants in these investigations. This was also the case in lower-temperature degradations.

The mechanism of cellulose pyrolysis after the formation of levoglucosan still remains vague. Berkowitz-Mattuck and Noguchi [28] proposed that fragmentation of levoglucosan through a free radical mechanism accounted for the observed gases, aldehydes, ketones, and unsaturated products. This mechanism although logical, has not been substantiated.

Tang and Neill [29] used differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in their studies concerning the effect of flame retardants on the pyrolysis and combustion of α-cellulose. Their TGA studies showed that flame retardants lowered the threshold temperature for pyrolysis and raised the char yield of the products. DTA studies in oxygen showed that although flaming was reduced, flame retardants often extended glowing. They explained that flame retardants cause the heat of combustion to be liberated over a wider temperature range and at a lower maximum intensity. Results of depolymerization and dehydration of cellulose and of polymerization and aromatization of pyrolysis products to a graphite-like char gave a reduced heat of pyrolysis.

In some of their most recent work, Tang and coworkers [30] postulated four major types of

reactions occurring in the pyrolysis from observations related to their DTA studies on wood cellulose. At 220 °C, cellulose undergoes a decomposition involving loss of water to yield a partially dehydrated species. Mass spectrometric thermal analysis confirmed loss of water. Depolymerization of the dehydrated species and volatilization of the resulting products begins at about 280 °C. In this process, previously untreated cellulose breaks into smaller fragments which are volatilized via an endothermic process competitive with the dehydration. The remaining reactions involve decomposition of the dehydrated cellulose via exothermic reactions into a number of gaseous products and residual char, and condensation of simpler substances from the decomposition products. Effective flame retardants are reported to minimize the depolymerization producing flammable tars (levoglucosan) and stimulate dehydration producing water and char.

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The Surface Pyrolysis Boundary Condition for the Combustion of Polymers*

R. F. McAlevy III** and W. S. Blazowski***

Combustion Laboratory, Stevens Institute of Technology, Hoboken, New Jersey 07030

The pivotal boundary conditions for polymer combustion involve the surface pyrolysis-vaporization characteristics. Generally, conditions at the burning surface (e.g., 500 °C or so) are so different from those encountered in classical bulk pyrolysis experiments that these data cannot be extrapolated reliably—data must be obtained at the conditions of interest. A critical review of experiments designed to produce such data, and the possible interpretations of these data are presented.

The authors have employed a combustion self-heating technique. In the experiment a planar diffusion flame is established between an axi-symmetric, "stagnation-point" flow of oxidant and the pyrolysis-product vapors emerging from the polymer surface lying below. The surface temperature, regression rate, and oxidant mass flow rate (the principal control variable) are measured. Recent results of this experiment are presented and discussed.

Key words: Combustion; flammability; kinetics; polymer burning; pyrolysis; rapid heating; surface pyrolysis; surface temperature measurement; thermal degradation.

1. Background and Introduction

The combustion behavior of polymeric materials that are incorporated into solid rocket propellants has been actively researched for more than a decade. It was assumed that better control of the rocket would be possible once this information was in hand. More recently, the combustion behavior of polymeric materials that are incorporated into fabrics, human habitats and vehicles has become a focus of attention. It is assumed that control of fire hazards would be possible once this information is obtained.

This paper reviews previous studies and describes a current study of the pivotal boundary condition common to all polymer combustion situations—the characteristics of surface decomposition-vaporization in response to intense surface heating.

During combustion of a polymeric material, decomposition-product vapors emerge from the surface and are burned with the oxidant component of the environment in a nearby flame. To produce ignition, an external energy source is required to initiate vaporization and the flame itself. Once ignition occurs at one site, the spreading of the flame to engulf adjacent surface locations is conveniently viewed as a continuous ignition process [1].[1] To become self-sustaining, some fraction of the chemical energy carried to the flame by emerging vapors must be fed back to the surface in the form of thermal energy to support further vaporization.

The combustion theorist formulates the detailed mass and energy balance appropriate for the situation of interest, and then attempts to solve the equations to predict ignition delay, flame spreading rate, steady-state deflagration rate (surface linear regression rate), etc. But in all cases, the pivotally important boundary condition is the surface decomposition-vaporization characteristics.

Conditions at the burning surface are outside the reach of equipment normally found in polymer research laboratories. Surface heating rates approaching a hundred cal/cm²/s produce surface temperatures of several hundred °C, subsurface temperature gradients approaching a thousand °C/mm, surface regression rates approaching a mm/s, and result in the subsurface material being heated to surface conditions at several hundred °C/s.

With other purposes in mind, for example negligible temperature gradients in test specimens, the typical polymer research laboratory employs "bulk heating" techniques—thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC)—which are designed to produce exposures far removed from typical combustion conditions. For example, extreme operations of such equipment results in a rate of temperature increase of only a few °C/s. And even though temperatures of a few hundred °C can eventually be reached, the lifetimes of the intermediary decomposition products are so much longer, vis-a-vis the combustion situation, that it is unrealistic to expect the same chemical path is followed in both cases.

For example, the temperatures at which important events occur, including melting, and charring, are generally not the same in both cases. And since the high surface viscous shear stresses of combustion situations cause "blow away" of the ubiquitous liquid-like layer at the surface of burning polymers, information concerning melting is of special interest.

Thus the combustion research community largely ignores the results of bulk heating decomposition experiments. Instead they attempt to determine the required information by means of experiments that produce conditions at the polymer surface which approximate combustion conditions. At the high surface heating rates employed in these experiments decomposition is restricted to the surface layer of polymer, with attendant steep temperature gradients. Frequently this is referred to as "surface pyrolysis". As the heated surface steadily regresses as a result of the exposure to heat, the term "linear pyrolysis" is employed interchangeably in describing the phenomenon.

Typical data are measured surface regression rate (r), and surface temperature (T_s). Due to the steep subsurface temperature gradients, and other complications, it has been found that unambiguous measurement of T_s is extremely difficult. Arrhenius plots of such data, that is, $\ln(r)$ versus $1/T_s$ are frequently presented, and the slope interpreted in terms of a "rate controlling" surface process, or "surface kinetics". Other models have been proposed that assume subsurface decomposition processes to be rate controlling. But the validity of all are open to serious question. Occasionally, correlations of r with surface heat flux are attempted to assess the energy required for vaporization—"surface energetics". Very rarely is the chemical composition of the emerging vapors measured.

This paper is intended to be a review of the experimental methods used to obtain polymer surface pyrolysis data, and to describe the current state of understanding of the process as well as a new approach to its study. The authors caution the reader that almost all existing data are of a quasi-steady nature, so that blind application to essentially unsteady combustion situations, such as ignition and flame spreading, could lead to erroneous prediction.

2. Review of Experimental Approaches for Investigation of Linear Pyrolysis

In this section some of the various techniques employed to obtain linear pyrolysis data will be discussed. These will be divided into categories determined by the principal mode of surface heating employed—conduction, radiation or convection, as well as controlled self-heating during combustion.

2.1. Conduction

The first attempts to obtain linear pyrolysis data were made by Chaiken [2] and others [3] over 10 years ago. They attempted to obtain surface kinetics data by means of a technique that involved forcibly pressing a polymeric strand against a flat, heated plate, termed the "hot-plate technique". Due to the intense surface heating rates so generated, linear pyrolysis rates approaching the range encountered in combustion situations were produced. A thermocouple placed in the plate was intended to measure the specimen "surface temperature".

This technique has several shortcomings: (1) The actual strand surface temperature is different from the measured plate temperature due to the presence of a thin vapor layer flowing between the hot plate and the vaporizing surface [4]; (2) if the surface decomposition process is influenced by the partial pressure of decomposition product at the surface, the presence of the solid hot-plate might produce conditions at the surface sufficiently different from those encountered during combustion to render the information useless as a realistic boundary condition for the combustion process [5][2]; and (3) the vigorously emerging vapor flowing across the specimen surface might produce "erosion" of the specimen [6], which would be especially serious if the material liquifies as it approaches the surface [7].

In an attempt to eliminate some of these shortcomings, a porous hot-plate was substituted for the solid hot-plate [8], and the device was employed to obtain data with inorganic materials. A one-dimensional gas phase theory has been developed to describe this experiment [9]. Empirically, large data scatter resulted even when subliming materials were investigated. Although, to the authors' knowledge, this technique has never been used to investigate polymeric materials, the high probability of the surface liquid layer flowing into the porous-plate prior to vaporization renders this technique quite unattractive for these materials.

In short, the conductive heating approach appears to have little future.

2.2. Radiation

Shannon [10, 11] and Lincoln [12] have exposed polymer specimens to radiant heating. A radiation furnace provided quasi-steady conditions while a "flash-tube" device was used to produce essentially unsteady exposures (e.g., exposure times of approximately 10 ms).

The basic drawbacks of this approach are that: (1) the radiation that passes through the surface and is absorbed in depth results in a subsurface temperature distribution much different than that experienced in a burning polymer, where internal radiation is generally negligible; (2) the fraction of the total incident radiation that passes into the surface is generally unknown since polymer surface spectral properties (i.e., reflectivity), are generally unknown at the conditions of interest; and (3) vapors emerging from the surface absorb an unknown fraction of the total radiation that would otherwise strike the surface.

The most encouraging aspect of the radiation

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[2] This effect is discussed in section 5.

heating method is the potential it holds for obtaining transient linear pyrolysis characteristics, but the drawbacks mentioned weigh heavily against it.

2.3. Convection

Thermoplastic materials have been subjected to intense convective heating by immersion in the exhaust of a small laboratory rocket motor [13]. In some experiments, the influence of environmental chemical composition was investigated by passing candidate gases up through specially-prepared, porous specimens, which then emerge at and bathe the heated surface.

As surface regression rate increases with increasing enthalpy of the impinging jet, substitution of electrical heating for the chemical conversion in the rocket motor—that is, the use of arc-jets [14, 15]—produces polymer regression rates approaching several mm/s [16]; approximately ten times greater than the typical maxima with the chemical rocket apparatus.

Convective heating appears to be superior to conductive and radiative heating techniques due to the fact that the experimental condition at the specimen surface is relatively well-defined, and there is ready optical access to it so that melting and charring can be observed.

The major drawback seems to be that the high velocity jet impacting and running over the heated surface can "blow away" liquid from the polymer surface melt layer. This additional mechanism for surface mass removal makes difficult determination of the actual surface decomposition-vaporization rate, and spuriously high values of this quantity are sometimes reported.

2.4. Self-heating During Combustion

A particularly useful form of surface heating utilizes a situation whereby the controlled combustion of pyrolyzed vapors above the surface provides heat feedback to drive the decomposition process. It possesses many of the advantages of the convective technique while oftentimes having a low velocity of external flow, and hence reduced influence on the melt layer.

Although mainly concerned with modeling a particular practical combustion situation, many studies of hybrid rocket motor characteristics [17, 18, 19] can be considered to be in this category of "self-heating" pyrolysis experiments. It is possible that parameters relevant to pyrolysis energetics could be obtained in this way. However, in most cases the flow in the combustion region was turbulent and could not be characterized in a fundamental manner. And thus surface heat flux predictions have an unacceptable element of uncertainty, which in turn is reflected in values of parameters extracted.

Other investigators [7, 20, 21, 22] have employed self-heating techniques involving better defined fluid mechanics. Simplistic attempts to calculate heat flux to the surface have been made [21, 22], but they have not been sufficient for accurate determination of surface energetics parameters.

Since surface heat flux depends on combustion of the pyrolysis product, self-heating techniques usually do not have as large a range of data as other techniques. The range of data in a self-heating method depends on the flammability limits of the particular system studied, while other techniques have limits depending on the ultimate output of the heating apparatus employed.

Finally, a significant drawback is that the surface pyrolysis characteristics of all polymeric materials cannot be investigated with these techniques. Some, such as Teflon, cannot be ignited and burned under ordinary conditions. Others which do ignite but char as they burn, such as acetate, make measurement of surface quantities (temperature, and even regression rate) very difficult.

3. Technique for Measurement of Important Quantities

The three principle quantities to be measured in surface pyrolysis experiments are the surface regression rate, surface temperature, and the heat flux to the surface. The regression rate measurement is readily accomplished by measuring the length of sample pyrolyzed in a given amount of time. Assuming the loss due to blow-away can be taken into account, it is a relatively simple quantity to determine. Surface temperature and heat flux determination pose much more difficult problems for the investigator. Techniques used for these measurements will be discussed in the following two subsections.

3.1. Surface Temperature Measurement

One common method of determining surface temperature is by means of an embedded thermocouple that is overrun by the regression surface. Errors are introduced by disturbances due to introduction of the thermocouple in the specimen—it is usually cemented together to hold the thermocouple in place. Thus the bead detects events in the cemented, rather than original, specimen. Errors are introduced due to the presence of the thermocouple in the subsurface temperature field—the different values of thermal conductivity of the metal thermocouple and specimen produce distortions of the heat flow and local temperature distribution patterns. The magnitudes of these errors are almost impossible to predict.

The embedded thermocouple technique has two other drawbacks: (1) steep temperature gradients below the surface may cause temperature differences of, typically, 100 °C across the thermocouple bead; and (2) the time-response of the thermocouple might introduce unacceptable errors in the rapid linear pyrolysis situations. The effect of each of these problems is minimized as the thermocouple size is decreased [23]. Thermocouples with bead diameters as small as 15 μm have been used [24, 25].

Although many investigators [23, 26, 27] have attempted to provide corrective schemes, the combined effects of all the errors (those due to mounting being perhaps the principal contributors) makes the embedded thermocouple technique unattractive.

Some data has been obtained by optically measuring the surface temperature [7, 13, 20, 28]. In these experiments infrared radiation emitted by the burning polymer in a specific wavelength band is recorded and compared to the radiation emitted by a blackbody source at known temperature. If the spectral properties of importance (surface reflectivity and material absorptance) are known, the measurement may be used to calculate surface temperature. These properties are not known at the temperatures of interest, so values obtained at lower temperatures must be used in reducing data.

This technique, however, can only be applied in the convective or self heating experiments. In conductive experiments the surface cannot be observed. In radiative heating experiments the possibility that some reflected radiation may be detected makes this technique generally unsuitable.

A possible drawback with this technique is that the hot gases between the sensor and the polymer surface may contribute to the radiation level detected. This is especially serious in the convective heating case employing rocket motor exhaust gases containing H_2O, CO_2, and CO, all of which can be strong emitters in the infrared wavelength regions of interest. With the self-heating techniques, combustion and formation of hot products occurs in a much thinner layer near the surface and its contribution can generally be neglected.

Simon [16] employed a novel radiative film technique for measurement of surface temperature. It involved use of a very thin film embedded in the polymer and oriented in the same plane as the regressing surface. Thermal radiation emitted by the film in the direction away from the pyrolyzing surface is measured and compared to a calibration, previously obtained at lower temperature, for the determination of surface temperature. The thin film (fractions of a micron in thickness) is silvered on the side facing the polymer surface and blackened on the side facing the sensor. Thus, it is not heated significantly by the radiation that impinges on it from the pyrolyzing surface, and it emits the maximum amount of radiation in the direction of the sensor. Although, because of the film's dimensions, problems of response, temperature difference, and lead loss are minimized with this technique, the complications due to the mounting technique are still encountered.

3.2. Heat Flux Determination

Surface heat flux is the other important quantity to be measured. Calorimetric techniques have been employed for this purpose with both the convective [13] and radiative [10] heating methods.

The amount of convective surface heating will be appreciably greater with the calorimeter in place because there is no "blowing" of pyrolyzed vapor
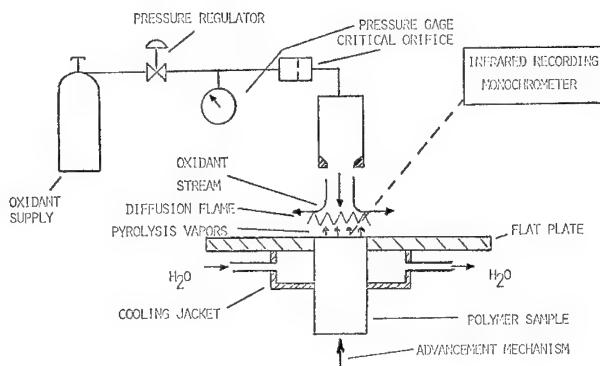

FIGURE 1: *Schematic representation of experimental apparatus.*

from the surface (a transpiration cooling effect) in this case. Various means of correcting the calorimetric data to compensate for this effect can be used, although they may require some questionable assumptions concerning composition of decomposition products, etc.

With radiation heating one must be concerned with the different reflectances of the calorimeter and polymer surfaces, as well as the absorbed radiation when pyrolyzed polymeric gases appear above the surface.

Measurements of heat flux in the conductive and self-heating experiments at present appear to be insuperably difficult to obtain. However, it is possible to model analytically the self-heating combustion situation to calculate the surface heat flux. This requires that the combustion region be well-defined and easily characterized fluid dynamically.

4. Surface Pyrolysis by Means of the Diffusion-Flame Technique

A self-heating experiment used by the authors to study polymer linear pyrolysis will now be discussed. In particular, a diffusion-flame technique is employed. In the experiment, a diffusion-flame is established between an axisymmetric flow of oxidant and the decomposition vapors emerging from the polymer surface lying below. Figure 1 is a schematic representation of the apparatus. An automatic advancement mechanism passes $\frac{1}{2}$ in diam. rods of the polymer specimen through a tight-fitting hole in a flat plate. The pyrolyzing surface is kept even with the flat plate which is a fixed distance ($1\frac{3}{8}$ in) from the oxidant nozzle ($\frac{3}{8}$ in diam.). A cooling jacket on the underside of the flat plate arrangement insures that no significant preheating of the sample will occur.

The oxidant mass flow rate $\dot{m}$ is regulated by controlling the pressure upstream of a choked orifice. The orifice had been calibrated by a standard flow meter. In most cases oxygen is used as the oxidant. In the remainder, oxygen is diluted with nitrogen, argon, or helium.

Temperature measurements are accomplished with the optical technique. The monitoring wave-
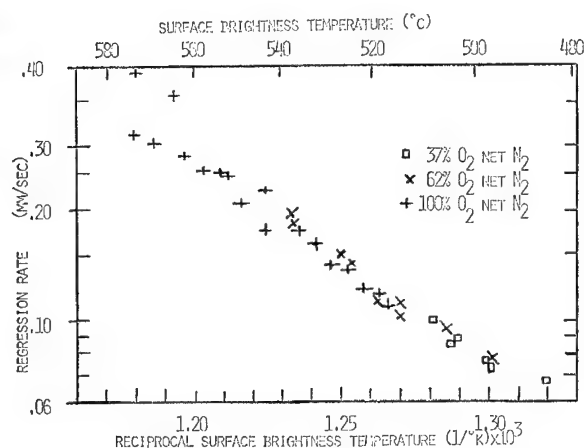
FIGURE 2: *Regression rate versus reciprocal surface brightness temperature for Delrin.*

length band is chosen to be one in which the absorption coefficient is high (typically 2,000 cm^{-1}). If this is so, and if the surface reflectivity is very low, the assumption of unity emissivity (i.e. calculating "brightness temperatures") may be made without causing significant error. Since accurate determination of these radiative properties at elevated temperatures (approaching those of the pyrolysis situation itself) constitutes a formidable problem, this laboratory's data has thus far been reduced to brightness temperatures only. A comparison between data taken at two separate wavelengths serves to check the brightness temperature values.

The previously mentioned problems that occur in self-heating experiments with materials that do not burn easily and with charring materials, certainly apply to the diffusion-flame technique. Although the range of data is not as extensive as in other techniques, regression rate did vary by a factor of 5 in most cases, (fig. 2).

The data may be presented in two plots. Kinetic data are typically shown on an Arrhenius plot as illustrated in figure 2 for Delrin (polyoxymethylene). The important parameter obtained with such a plot
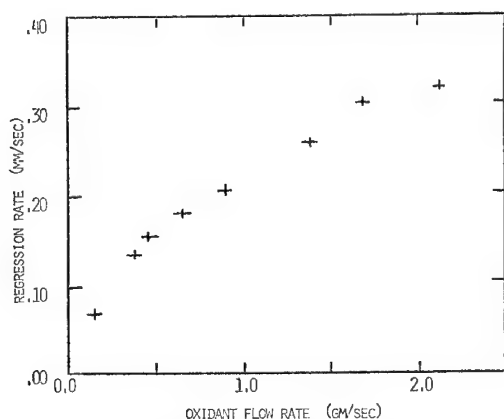

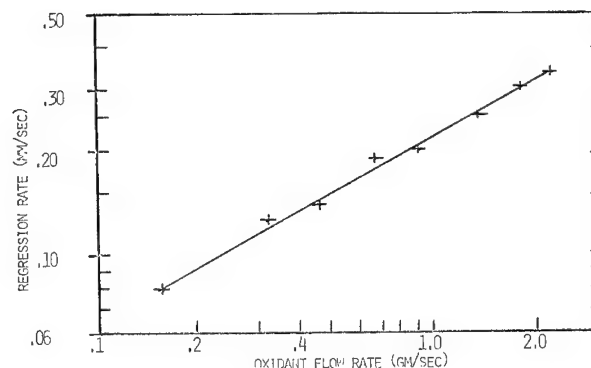FIGURE 3: *Regression rate versus oxidant flow rate for PMM with 100 percent oxygen.*

FIGURE 4: *Log-log plot of data from figure 3.*

is the apparent activation energy for a surface process.[3] Delrin, for example, exhibits a value of approximately 23 kcal/mole. Note that the changing oxidant composition does not seem to affect the Arrhenius correlation of these data.

Empirical values concerned more with the energetics of surface decomposition are plotted as regression rate versus oxidant mass flow rate. Such information is shown for polymethylmethacrylate (PMM) in figure 3. A power-law correlation (i.e. expressing the data in the form $r = \alpha \dot{m}^\beta$) for such data may be performed on a plot of log regression rate versus log oxidant flow rate, as shown in figure 4. Results of such a correlation for some polymers are shown in table 1.

TABLE 1. *Empirical power law ($r = \alpha \dot{m}^\beta$) parameters*

Material	α(mm/s)	β
Plexiglas	0.23	0.51
Plexiglas 55	.22	.53
Nylon 6–6	.24	.46
ICRPG binder (polyurethane)	.28	.44
Delrin	.22	.48
Polystyrene	.17	.53
Polypropylene	.23	.67

A theoretical analysis of the experimental situation is required for the extraction of energetics parameters from measured values of α. Recently an analysis has been produced [29] that goes beyond the unrealistically simple efforts of the past [21, 22].

The combustion situation is modeled by an axisymmetric boundary layer flow where combustion is assumed to occur in an infinitesimally thin "diffusion-flame". The analysis requires specification of oxidant composition, surface heat of gasification, heat release per unit mass of fuel reaching the flame, and the stoichiometric ratio for the appropriate combustion products. The last two quantities describe the gross details of the chemical reaction at the flame.

Besides providing a basis for the interpretation of α values for the evaluation of energetic param-

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[3] The bases for rationalizing pyrolysis data will be discussed in the next section.

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eters (i.e. surface heat of gasification), the analysis predicts values for surface concentration of decomposition vapor. This concentration may be varied by changing the oxidant composition, as was done in generating the Delrin data for figure 2. In this way the influence of the decomposition product partial pressure at the surface on the decomposition process can be checked. In the Delrin example, no significant effect is observed.

The analysis predicts that the regression rate should vary as the square root of oxygen impingement rate (i.e. $\beta = 0.5$). Comparison with table 1 shows that all experimental values of this quantity are reasonably close to the predicted value except that for polypropylene. Significant deviation from $\beta = 0.5$ may indicate a change in the energetic requirements of the degradation-vaporization process, and hence, in the process itself, according to the theory.

A future publication [30] will contain the kinetic and energetic polymer data obtained with this experiment. Further description of the experiment and technique, including enlightening photographs of the pyrolyzing surfaces during combustion also will be contained therein.

5. Theoretical Foundations for Data Interpretation

This section will concern different ways in which linear pyrolysis data can be interpreted, based on different assumed models of the actual mechanism.

Many investigators [31–34] have attempted to rationalize linear pyrolysis data on the assumption that the thermal degradation which occurs in a subsurface reaction zone is the rate-limiting step.

Shteinberg and Sokolova [31] point out that this situation is very similar to the classical case of gaseous reaction front propagation. So that for a "zeroth" order reaction, the apparent activation energy of the process will be approximately half the isothermal bulk activation energy value. And these authors offer this as a first approximation of the polymer linear pyrolysis problem.

Rabinovitch [32] used an assumed subsurface temperature profile coupled with the assumption of a first order degradation process to derive an integral expression which correlates the surface temperature, surface regression rate and the first order process activation energy and frequency term. The assumed temperature profile which is for the case of constant surface regression rate (where the pyrolyzing polymer is considered to be a semi-infinite, inert solid with constant properties) follows the relationship [35]

$$\frac{T(x) - T_0}{T_s - T_0} = \exp\left(-\frac{r}{a}x\right) \tag{1}$$

Where:

x is the distance beneath the surface.
$T(x)$ is the temperature at position x within the solid phase.

T_0 is the temperature of the solid far from the surface.
T_s is the surface temperature.
a is the thermal diffusivity of the solid, assumed constant.
r is the surface linear regression rate.

Since the subsurface decomposition reaction will involve a heat of reaction, eq (1) is not an accurate representation of the temperature profile. An improvement on the Rabinovitch model, then, would include a heat of reaction term in the analysis. This ameliorative step, however, requires a much more complicated analysis.

Lengelle [36] accounted for subsurface reactions by employing a matched asymptotic expansion scheme. The outer expansion (for the region away from the surface) takes into account only the conduction heat transfer, while with the inner expansion (the region close to the surface), the heat of reaction term is taken into account also. A more accurate mass conservation expression was also used in this model.

Another common method of explaining pyrolysis data involves the assumption of an unopposed surface reaction [2, 13]. In this case correlation of data is accomplished by employing the following relationship

$$r = A_1 T_s e^{-E_a/RT_s} \tag{2}$$

where A_1 is a constant, R is the gas constant, and E_a is the apparent activation energy of the surface decomposition process. This equation will give nearly a straight line in a log r versus $1/T_s$ plot (the linear T_s dependence is weak and often neglected). If data plotted on these same coordinates results in a straight line, empirical values of A_1 and E_a may be found.

As Barrere and Williams [5] point out, however, it is also possible that equilibrium conditions for the decomposition process apply at the surface. If this boundary condition is to be used, the following relationship must be satisfied.

$$\prod_{i=1}^{n} (C_i^{\mu_i''}) = K_s \tag{3}$$

where μ_i'' is the stoichiometric coefficient for decomposition vapor species i, C_i the surface concentration of species i, and K_s the equilibrium constant for concentrations.

Naturally the surface process can also be intermediate between the two extremes of unopposed and equilibrium surface gasification. If this is the case, the following relationship governs the decomposition rate

$$r = A_2 T_s \exp\left[-\frac{E_a}{RT_s}\right]\left\{1 - \frac{PX}{P_1}\right\} \tag{4}$$

where A_2 is a constant, P is the total pressure, P_1 the equilibrium vapor pressure corresponding to T_s, and X the mole fraction of decomposition vapor at the surface.

Equation (4) illustrates a possible hazard of

directly applying pyrolysis data to combustion situations. In many cases (such as the hot plate and arc jet) total pressure or mole fraction of the decomposition vapor at the surface may not be controllable or known.

6. Comparison Between Data and Theoretical Foundations

The various techniques employed have generally yielded conflicting data. Lack of a standard test material makes difficult establishment of their relative validity—each experimenter used a different material. For reasons previously discussed, the authors believe that their diffusion-flame technique will yield data that is well characterized and contains less error than that of previous data. At this writing insufficient data has been produced to allow an unambiguous evaluation of the technique.

Without reliable data, evaluation of the various theoretical approaches is a futile undertaking. Once sufficient data is available, however, the investigation of model validity will still be complex, for there is no reason to expect that one model will be suitable for all polymers. Much more work is required in this area.

7. Summary

After reviewing the known linear pyrolysis techniques the authors have decided in favor of the diffusion flame technique. Perhaps further work with this technique will yield information useful in the explaining of discrepencies which now exist among the data generated by the many types of surface pyrolysis experiments employed in the past.

A number of theoretical approaches to data interpretation have been presented. Since past data have been in serious disagreement, they cannot provide a basis by which the validity of these models may be evaluated.

Perhaps one of the causes of discrepencies in the data is that different experimenters have employed different materials in their investigations, and it appears no common material was ever tested. For example, polymethylmethacrylate data are reported by a number of experimenters [2, 3, 7, 10, 16] but some prepared it in their own laboratories while others obtained it from different commercial sources. Thus, there was no control on curing, etc., and fine comparison and interpretation of the resulting data is unwarranted at this time.

The establishment of a standard testing material can be invaluable in helping experimenters calibrate their equipment, etc. This is a necessary action which must be taken if the various techniques, and thus the quality of the data produced, are ever to be meaningfully evaluated. The authors suggest that the National Bureau of Standards take a leadership position in this endeavor.

Once polymer surface pyrolysis is understood it will be possible to design polymers for many specific combustion related purposes. For example, material designed to be fire resistant may make use of the release of bromine, or some other known fire retardant [37], during the decomposition process. So a rational control of polymer pyrolysis properties can lead to many improvements in materials for use in solid rocket propellants, fabrics, building materials, and many other applications where their combustion behavior is of interest.

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Discussion

W. C. Kuryla (Union Carbide Corporation):

I wonder if Dr. McAlevy or Mr. Alger could explain why in certain cases a two second ignition time in the AATCC standard vertical flame test yields a completely burned fabric while the same fabric after exposed to a 12 second ignition time burns only half the way before it extinguishes? What are the important physical as well as chemical factors which control this particular situation?

Raymond Alger:

While I cannot explain Dr. Kuryla's observation regarding the effects of ignitor time on the AATCC tests, I am interested in what attempts have been made to resolve the question. Two effects of the 10 extra seconds of heating would appear to be a change in the sample environment, particularly the atmosphere in the box and a change in the fuel. The atmosphere could be altered both by the combustion products from the torch and the increased sample combustion and pyrolysis products. While fuel modification is not a very plausible reason for the observed effect, the longer heating time will generate more pyrolysis products which can escape and leave the fuel changed. If the atmospheric environment is responsible, the effect should vanish when the box is removed. On the other hand, alteration of the fuel should be independent of the box.

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

A symposium on The Mechanisms of Pyrolysis, Oxidation, and Burning of Organic Materials was held at the National Bureau of Standards in October 1970. This volume contains the nineteen papers presented and much of the discussion which followed.

These papers review and discuss the current status of kinetic studies on the reactions of organic materials in both gas and condensed phases. The topics covered include: pyrolysis of hydrocarbons, pyrolysis of polymers, oxidation of polymers, oxidation of organic compounds, burning of organic compounds and burning of polymers. Particular emphasis is placed on the elucidation of the mechanisms of reaction in terms of free radicals or other transient species and physical effects.

17. KEY WORDS (Alphabetical order, separated by semicolons)
Burning; hydrocarbons; organic materials; oxidation; polymers; pyrolysis.